

The autothermal reforming of artificial gasoline

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THE AUTOTHERMAL REFORMING OF ARTIFICIAL GASOLINE

PRAHARSO

A dissertation

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Abstract

Stringent legislation on control of vehicle exhaust emissions has led to consideration of alternative means of reducing emissions, with hydrogen fuel cell powered vehicles being accepted as one favoured possibility. However, the difficulties of storing and distributing hydrogen as a fuel are such that the conversion of more readily available fuels to hydrogen on board the vehicle may be required.

The production of hydrogen by the partial oxidation of isooctane over Rh/Al₂O₃, Rh/CeO₂- δ Al₂O₃ and Rh/CeO₂-ZrO₂ catalysts has been investigated. Oxidation was initiated at temperatures between 200 – 220 °C. The yield of hydrogen was 100%. CeO₂-ZrO₂ was found to be the best support.

The production of hydrogen by the autothermal reforming of artificial gasoline has been studied. Part of gasoline is oxidised to produce heat and steam to promote the steam reforming of unburnt gasoline to produce hydrogen. The use of platinum impregnated on ceria supports (active for oxidation) and a commercial nickel based catalyst (Ni-com), for steam reforming of gasoline have been explored.

Initiation of oxidation of artificial gasoline over unreduced platinum based catalysts occurred at temperature as low as 150 °C, depending on the oxygen:carbon ratio and the liquid hydrocarbon used.

Detailed kinetic studies of the steam reforming of isooctane and artificial gasoline (a mix of cyclohexane, isooctane and octane) over pre-reduced Ni-com catalysts showed that the reaction was 0.17 order in isooctane and 0.54 order in steam, whilst the reaction was 0.08 order in artificial gasoline and 0.23 order in steam.

Mechanisms have been proposed to account for the dual site surface reaction with dissociative adsorption of isooctane or artificial gasoline and steam.

Combined oxidation and steam reforming systems (autothermal reforming) using Pt/CeO₂ as a front catalyst bed and Ni-com as the rear bed at the feed conditions of oxygen:carbon (O:C) ratio of ca.1.2 and steam:carbon (S:C) ratio of ca.2, produces ca. 3.5 moles of hydrogen per mole of gasoline fed. The system reaction temperature could be controlled by adjusting the O:C and S:C ratios in feed.

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Chapter 1 Introduction

The number of cars in the world is predicted to double from 400 million to 800 million in the next twenty years [1]. Such a rapid growth is responsible for the problem of localised pollution of poor air quality or photochemical smogs [2]. Catalytic converters involving three-way catalysts have been developed and fitted into car exhaust systems for more than two decades in order to oxidise hydrocarbons and carbon monoxide, and to reduce nitrous oxide to nitrogen [3].

Increasingly stringent environmental regulation of pollutant emissions such as EPA Tier II and California Zero Emission Vehicle has led to the development of engines that produce much less pollutants [4, 5].

Four key areas have been identified involving direct injection compression ignition engines, hybrid electric vehicles, fuel cell powered electric vehicles and the use of light weight materials to better control vehicle emissions [4]. However, fuel cell systems are receiving increasing attention world wide as more efficient and more environmentally friendly energy devices, with the proton exchange (or polymer electrolyte) membrane fuel cell (PEMFC) being identified as the optimal unit for transport applications, despite the fact that they have the disadvantage of operating on hydrogen as a fuel. Since distribution of hydrogen is difficult and storage of hydrogen in a vehicle adds weight, consideration has been given to the conversion of more readily available fuels to hydrogen on- board the vehicle [4-8].

Most cars rely on liquid fossil fuels, especially gasoline, which has a high energy density and wide distribution network. As a result, liquid hydrocarbons are promising as fuels for on-board applications, despite the fact that they often contain sulphur compounds that have to be removed due to their detrimental effect on catalysts in a fuel processing device. Alcohol fuels, on the other hand, have the advantages of being almost sulphur-free and are easier to reform at lower temperatures, but poor distribution network and the resultant lower energy density make them less attractive compare to liquid hydrocarbon fuels [6] .

Recent progress in desulphurisation technologies for liquid hydrocarbons [9, 10], coupled with a readily available wide distribution infrastructure for gasoline, would suggest that gasoline is a promising candidate for hydrogen generation on-board the vehicle, whilst the combination of oxidation and steam reforming (autothermal reforming) is a preferred process [4]. This option forms the basis of the present study.

The ultimate goal of the study would be to produce design data for the production of hydrogen from gasoline on board a vehicle, since – in the long run – this will be required. However gasoline consisted of a wide range of hydrocarbons with similar boiling points and the scientific investigation of such a system would be complicated by cross over effects from the different components. As a result, a decision was made to focus the study on a model mixture. This artificial gasoline contains representatives of all gasoline components as originally described by Duffy and Nelson [11]. The components and the amounts present in the mixture is described in Chapter 6. Since previous studies have successfully demonstrated the feasibility of autothermal reforming of light hydrocarbons at ambient temperature with the aid of hydrogen/air or methanol/air mixtures as initiators [12], the

feasibility of autothermal reforming of artificial gasoline at ambient temperature in the absence and presence of any initiator is also considered.

Overall, the study has focused on the processes of oxidation and steam reforming of artificial gasoline, inclusive of the preparation, characterisation, selection and testing of catalysts. The kinetics of steam reforming of isooctane and artificial gasoline (mixtures of cyclohexane, isooctane and octane) have been investigated and the results are employed to examine the system and operation of autothermal reforming.

In order to lay the foundation for the experimental work and subsequent data interpretation, Chapter 2 provides the literature background to the subject of hydrocarbon oxidation, steam reforming and autothermal reforming. Issues related to catalytic mechanisms, kinetics and coking are addressed. Chapter 3 deals with the rationale for specific experimental requirements and the overall system analysis. In Chapter 4, catalyst synthesis and characterisation results are discussed. Sol-gel and multiple impregnation methods were used. Characterisation of catalysts by BET (total surface area), TPR (temperature programmed reduction) – TPO (temperature programmed oxidation), and hydrogen chemisorption was carried out. Chapter 5 discusses the partial oxidation of single hydrocarbon over rhodium-based catalysts. In Chapter 6, oxidation of artificial gasoline over a platinum-based catalyst is presented. Chapter 7 and 8 deal with steam reforming of artificial gasoline and in Chapter 9, autothermal gasoline reforming was investigated. Conclusions and recommendations are given in Chapter 10.

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Chapter 2 Literature review

2.1 Introduction

Hydrogen is a vital commodity in many chemical and petroleum processing operations and is also a clean energy source. Refineries and chemical companies use hydrogen to produce commodity, fine and specialty chemicals such as toluene-diamine, hydrogen peroxide, ammonia, pharmaceuticals, and synthesis gas. The steel industry uses hydrogen for steel annealing. The food processing industries use hydrogen for the hydrogenation of fats and oils. Most of the hydrogen is produced by catalytic processes, involving many steps with various catalysts. There is an increasing demand for economical and environmentally-safe production of hydrogen both for stationary and for vehicular applications [1-3].

In the petrochemical industry, steam reforming, partial oxidation and autothermal reforming processes have been developed, while on-board fuel cell technology using hydrogen is considered an attractive choice for automobile and other vehicular applications [2-7]. Some alternative ways of producing hydrogen which include use of methane, use of membrane reactors, solar energy for electrolysis of water, and conversion of biomass have also been reviewed [1].

With respect to environmental catalysis, the control of vehicle exhaust emissions using catalytic converters has been widely studied [8]. However, increasingly stringent legislation

has led to consideration of alternative means of reducing emissions, with fuel cell powered vehicles being considered as one favoured possibility [2]. The optimal unit for transport applications has been found to be the polymer electrolyte membrane fuel cell (PEMFC) but these cells have the disadvantage of operating only with hydrogen as a fuel. Since the distribution and on-board storage of hydrogen presents very real problems [2], attention has been focused on the conversion of more readily available fuels to hydrogen on-board the vehicle.

In general, higher hydrocarbons such as LPG and gasoline offer better hydrogen yields than methane but are less popular, due to the possibility of coke formation during hydrogen production. However, because they are more easily transportable and readily available, they deserve more serious consideration especially for non-stationary applications.

This has led to the focus of the present work on fuels conversion for the production of hydrogen on-board a vehicle.

2.2 The principles of fuel cells

Overviews of fuel processing for fuel cells have recently been published [9, 10]. Fuel cells are much more energy-efficient, and could achieve as high as 70-80 % system efficiency in electric power plants using solid oxide fuel cells (SOFC), in comparison to the current efficiency (30-37%) of combustion process. They also offer 40-50% efficiency for transportation using proton exchange membrane fuel cells (other authors quote polymer electrolyte membrane fuel cells-PEMFC [2]) or solid oxide fuel cells versus the current

efficiency of 20-35% [10] (other author quotes ~10 % [11]) using an internal combustion (IC) engine.

The concept of the fuel cell was first discovered by Sir William R. Grove in 1839, who used hydrogen and oxygen as fuel for catalysis by platinum electrodes [10, 12]. A fuel cell is an electrochemical device in which the chemical energy stored in a fuel is converted directly into electricity. It consists of an ion-conducting electrolyte material which is inserted between two thin electrodes, namely a porous anode and cathode. The inlet fuel passes over the anode (negatively charged electrode) where it catalytically splits into electrons and ions. Oxygen passes over the cathode (positively charged electrode). The electrons go through an external circuit to provide an electric load while the ions move through the electrolyte toward the oppositely charged electrode. At the electrode, ions combine to create by-products (water and carbon dioxide). Thus, fuel cell produces DC electricity due to the electrons flowing from the anode to the cathode [10].

The PEMFC operation is represented by the following reactions occurring on Pt-based electrodes at temperatures between 70 and 90 °C [10, 13]:

Anode (fuel) reaction : $\text{H}_2 \leftrightarrow 2\text{H}^+ + 2\text{e}^-$

Cathode (oxidant) reaction : $\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2\text{O}$

Overall reaction : $\text{H}_2 + \frac{1}{2} \text{O}_2 \leftrightarrow \text{H}_2\text{O}$

As long as fuel is fed, fuel cells will continuously produce electricity [10].

2.3 Basic fuel conversion

Fuel cell vehicles are undergoing extensive research and development, primarily due to their energy efficiencies and low emissions. Hydrogen is the ultimate fuel to power such vehicles. Since an infrastructure for wide distribution of hydrogen is not yet available, on-board processing of liquid fuels is considered as a promising choice [4, 6, 13-20].

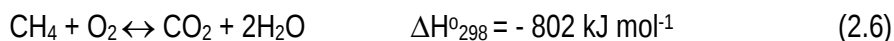
Fuels conversion by thermal decomposition, steam reforming, partial oxidation, and autothermal reforming have been reviewed [19]. Thermal reforming requires high energy to dissociate the fuel. Apart from hydrogen, carbon is also produced, and the reaction is not preferred for the production of hydrogen [2, 21-23].



Steam reforming of alcohols and hydrocarbons produces hydrogen and carbon oxides according to the following reactions [3]



Reactions (2.2) to (2.4) are endothermic and require an external heat supply. In the context of an on-board hydrogen processor, the heat can be supplied by combusting part of the fuel into carbon dioxide and steam [23]



The mixed reaction of oxidation (2.6), steam reforming ((2.2) to (2.4)) and water gas shift (2.5) is defined as *indirect partial oxidation* [2].

Steam generated by reaction (2.6) is usually insufficient to carry out steam reforming and additional water may be injected to the reactor [3]. Moreover, steam reforming is thermodynamically favoured at high temperatures where carbon deposition may occur. Thus, the amount of water added should be enough to suppress coke formation [24].

Direct catalytic partial oxidation may appear as the ideal solution to produce hydrogen, but the ratio of hydrogen/carbon monoxide is lower as compared to steam reforming [2, 3]



However, if reaction (2.7) is coupled to reaction (2.5), more hydrogen may be obtained.

From thermodynamic simulations, direct partial oxidation is favoured at high temperatures (ca. above 825 °C) in excess of hydrocarbon [23]. Moreover, short contact times of the order of millisecond are required [25], since longer contact times or post reactions will favour either indirect partial oxidation or dry (CO₂) reforming of hydrocarbon [2].

Although direct partial oxidation involves the advantage of very fast reactions (and thus requires smaller equipment), a significant problem may occur due to the fact that total oxidation can also occur and can cause flames and explosions [25].

In the following sections, indirect partial oxidation and direct partial oxidation will be discussed in more detail. It should be noted that catalysts used in both systems are prone to catalyst deactivation either due to poisoning or thermal sintering [22]. In the context of fuels for PEMFC, levels of carbon monoxide of above ca. 10 ppm will poison the electrodes [10, 26]. Therefore, the methods of reducing carbon monoxide to below these levels must be incorporated in designing any fuels conversion system.

In subsequent sections, the individual reactions of oxidation (both total and partial oxidation) and steam reforming will be discussed, followed by autothermal reforming-combined reactions. More attention will be focused on the conversion of higher hydrocarbons.

2.4 Catalytic oxidation of fuels

Fuel oxidation plays an important role in supplying heat for driving steam reforming reaction in autothermal systems. This is attained by oxidising part of the fuel. Catalytic oxidation of hydrocarbons is rarely initiated at ambient. As a result, a more reactive substance such as methanol or hydrogen is oxidised to heat the system to a certain temperature where the oxidation of hydrocarbons is initiated (light off) [27]. Once the total

oxidation of part of the hydrocarbon is initiated, the heat and steam produced is used for steam reforming.

Catalytic oxidation can be accelerated by using precious and transition metals, their alloys, metal oxides, carbides and some other substances [28].

Besides autothermal reforming, direct catalytic partial oxidation is also considered as an alternative route for the production of hydrogen from fuels. This particular process will be reviewed first, and subsequently followed by total oxidation. Fuels to be discussed involving hydrogen and methanol in the context of an initiator for autothermal reforming, and hydrocarbons, where the attention is more focused on the combustion of gasoline-like hydrocarbons.

2.4.1 Direct catalytic partial oxidation as a source of hydrogen

Direct catalytic partial oxidation (DCPO) is considered as a dream reaction, since DCPO, for example of methane, involves a very low heat of reaction. To produce one mole of CO and two moles of H₂, methane partial oxidation exhibits ΔH^0_{298} of -38 kJ mole^{-1} , which is comparable to the heat of reaction of water gas shift (-41 kJ mole^{-1}) [3]. However, the ratio of H₂/CO of 2:1 is less than optimal in the context of fuel cell applications [2].

Partial oxidation of methane has been extensively studied [29-33] due to its high H:C ratio [34], and perhaps due to the lower tendency to coke formation in comparison to higher hydrocarbons. Early work on partial oxidation of methane was carried out by Prettre et al. [29] over a 10% Ni catalyst with a mixture of methane to oxygen ratio of 2:1 in the

temperature range 725 – 900 °C and at contact times of 6-42s. Essentially, complete conversion of methane was observed at above ca. 900 °C. Although, the outlet reactor gas composition was in agreement with thermodynamic calculations based on the exit catalyst bed temperature, direct partial oxidation was not observed. Based on the temperature profiles along the catalyst bed, it was suggested that the reaction proceeded in two steps. First, a complete combustion of part of the methane fed at the expense of all oxygen supplied (exothermic), followed by steam and/ or carbon dioxide reforming of unburnt methane (endothermic).

Ashcroft et al. [30, 31] were the first to employ Ru supported on rare-earth oxides and several transition metals (Pt, Rh, Ru, Ir) in addition to Ni, supported on Al₂O₃ catalysts for partial oxidation of methane. Working at high temperatures (ca. 750 °C) and short contact times (ca. 0.1 s) with mixed feed (CH₄:O₂:N₂ = 2:1:4), they reported CH₄ conversions above 90 % and H₂ selectivities of 95 - 99%. The conversions and selectivities decreased as the contact time decreased. In agreement with Prettre et al., the reactions mechanism involved indirect partial oxidation.

Schmidt et al. [11, 25, 34-54] have explored DCPO of various hydrocarbons (including gasoline-like fuels), on noble metals coated honeycomb catalysts, and limited work on DCPO of methanol. Their investigations were based on the concept of millisecond chemical reactions and short contact time chemical reactors where temperatures were determined by inlet parameters only. Performance was claimed to be nearly unchanged over wide variations in flow rate and highly non equilibrium products could be obtained at high conversions. High temperatures are mandatory for significant reaction to occur in 10⁻³ sec. Their studies involved a steady state approach to optimise hydrogen production, and a transient approach to attain fast light off. For steady state investigations at short contact

times (1-10 ms) and at C:O ratio of 1, almost complete conversions of individually tested hydrocarbons (C_1 - C_{10}) were observed. While hydrogen selectivities of C_1 - C_8 were reported to be above ca.95%, the hydrogen selectivity of C_{10} was lower (~70 %). This was attributed to cracking of decane to lower hydrocarbons (olefins) [34] but, surprisingly, no carbon formation was reported. Limited work on DCPO of isooctane/toluene mixtures (75/25) lowered synthesis gas yields to below ca. 70% due to olefin by products. An attempt to use gasoline as fuel poisoned the catalyst after several hours of operation [48].

With regard to their transient experiments, the light off of methane (~600 °C [55]) and octane (~200 °C [48]) were attained between 3 – 13 s depending on the flow rate employed (ca. 2000 to 9000 mL min⁻¹ of air); the higher the flow rate, the shorter the time to reach light offs. While light offs of methane and octane were clearly observed, it was not discussed why the light off of butane was unknown.

In the context of an on-board fuel processor for a PEMFC, attaining light offs in few seconds is advantageous, but obtaining such high flow rates in short times is another question. It is interesting to note that, to achieve light offs, a spark was used to initiate the homogeneous combustion of fuel/air mixtures in a “combustion chamber”, and the blue colour of the combustion flame along with carbon oxides observed by a mass spectrometer were used to confirm coke formation free operation. No decoking experiments of spent catalysts were reported. Furthermore, rhodium was found to be the best catalyst, but with a relatively high loading (ca. 5%).

Even though light offs of individual hydrocarbons were extensively studied, no further investigations of hydrocarbon mixtures (except for isooctane/toluene mixtures) were carried out. As will be discussed in later sections, light offs of hydrocarbon mixtures involve

competitive adsorption of individual compounds, which, in turn, may give a different result in comparison to a single compound.

A similar approach of using millisecond contact times was adopted by Choudary et al. [56]. Partial oxidation of methane was carried out over a reduced nickel based catalyst supported on alkaline earth oxides. Employing undiluted feed (methane: pure oxygen = 1.8:1) and a contact time of 1 ms, 87 % methane conversion was reported at 700 °C, whilst hydrogen selectivity of 95 % was observed. A hydrogen/carbon monoxide ratio of 2.0 in the products was also observed.

Mallen and Schmidt [57] have extended studies to methanol decomposition and DCPO over Pt and Rh foils: methanol conversions were much lower compared to methane. Methanol decomposition was significant at about 530 °C over Pt and 280 °C over Rh, while extensive conversion was observed at about 630 °C on both foils. For methanol oxidation over Pt, combustion products were observed between 180-430 °C whilst oxygen was reported to bind strongly over Rh even at elevated temperatures. In contrast to the conversion for methanol decomposition (ca. 30 %), the maximum conversion for methanol oxidation over both foils was ca. 0.3%. The reasons for the change in conversion between the two reactions was not clearly discussed.

Hydrogen produced by DCPO can be maximised if the system is combined with the water gas shift reaction (WGS). Working over an Rh-based catalyst in the first reactor, Maiya et al. [58] carried out the partial oxidation of methane at 900 °C to produce 2 moles of H₂ per mol of CH₄. The hydrogen and carbon monoxide produced was then subjected to the WGS reaction in a second reactor over a Cu/Zn catalyst. At ca. 400 °C and a steam/CO ratio of

ca.2, the hydrogen produced was in agreement with the thermodynamic prediction (2.9 moles H_2 per mole of CH_4 consumed).

Schmidt et al. [45] have extended the DCPO-WGS system for isooctane over Rh-coated monoliths at millisecond contact times. Steam was injected in the system at steam:carbon ratios from 1 – 8 with the reaction temperature was set at ca. 700 °C. A second rhodium WGS catalyst was placed behind a rhodium partial oxidation catalyst. Lowering the CO ratio to less than 10 % was claimed, but the CO ratio was not clearly defined. While Maiya et al. compared the amount of hydrogen produced per mole of hydrocarbon consumed to the values calculated by thermodynamics, Schmidt et al. did not report the hydrogen selectivity after WGS experiments.

In comparison to steam reforming, DCPO has some advantages of autothermal reaction, including rapid response, smaller reactors [25] and the possible absence of coke formation [2], but the product $H_2:CO$ ratio is lower than the ratio produced by steam reforming. Moreover, it may suffer from flammability problem. Mixtures of air and fuel are close to the homogeneous flammability limits, and any variation as a result of pulsing of liquid hydrocarbons feed may cause a flame or even an explosion [54].

2.4.2 Catalytic total oxidation

Fuels combustion is an exothermic reaction and the liberated heat can be utilised to drive endothermic steam reforming for the production of hydrogen. Synthesis gas can also be produced by the partial oxidation as previously discussed. However, neither steam

reforming nor the partial oxidation reaction is significant at ambient temperature. Thus, it is necessary to raise the reactor temperature to a certain level where either steam reforming or partial oxidation is initiated. This is determined by fuels reactivity and catalysts activity. Hydrogen [59] and methanol [60] will oxidise at ambient over a pre-reduced noble metal catalyst, and it may be possible to heat the reactor to the light off temperature of higher hydrocarbons by this route [27, 61, 62].

The use of a battery to provide electric heating to the system is also viable, though a powerful battery is mandatory and fuel consumption for electric charging is inevitable. Therefore, fuel catalytic combustion is considered as the preferred option to pre-heat the reactor [2].

2.4.2.1 Oxidation of hydrogen

Hydrogen is a clean energy source which produces steam upon combustion. The flammability limits of hydrogen are between 4 to 75 % in air and 4 to 94 % in oxygen [63]. The catalytic combustion of hydrogen is well documented [4, 63-67]. Hydrogen ($\text{H}_2:\text{O}_2 = 3.7:1$) lights off at ambient temperature on $\text{Pt}/\delta\text{-Al}_2\text{O}_3$. Depending on the feed concentration, the bed temperature rises to a certain value. The maximum bed temperature could be more than 350 °C [27, 59, 67-69].

2.4.2.2 Oxidation of methanol

The combustion of methanol and of products generated from methanol fuelled vehicles has been investigated over Pt wire [70], over supported Rh, Pd, Pt, Ag, Cu-Cr and over Pd-Ag

based catalysts [70-72]. In methanol-lean feeds, HCOH, CO₂, and H₂O were the only products, while in methanol-rich feeds, CO, H₂, HCOH, CO₂, and H₂O were observed over Pt wire. In the absence of CO, supported monometallic Pt and Pd exhibited the highest activity and CH₃COOH was observed, but the reaction was strongly inhibited by CO. The bimetallic Pd-Ag catalyst showed greater CO and methanol oxidation activity than either of the single Pd or Ag catalysts.

Jiang [60] carried out catalytic methanol combustion studies over supported Pt and Cu catalyst in the absence and presence of water. When samples were pre-reduced, both catalysts oxidised methanol at ambient, but in the oxidised state, they became active at about 200 °C. Whilst Mc. Cabe et al. [60, 70-72] reported partial oxidation at lower temperatures, Jiang [60] observed only carbon dioxide and water as combustion products.

2.4.2.3 Oxidation of hydrocarbons

The combustion of fuel in the gas phase is a very important process, the reaction producing heat, carbon dioxide and water. However, gaseous pollutants such as nitrogen oxides, carbon monoxide etc. can also be produced. In contrast, catalytic oxidation is usually more efficient.

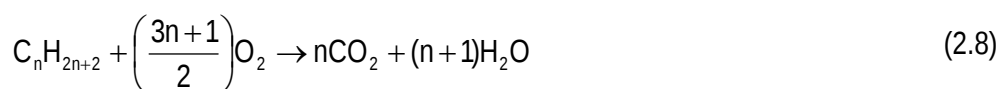
Some indication of the reactivity of a hydrocarbon can be obtained by measuring the temperature at which the catalytic oxidation becomes significant (light off temperature, LOT). LOT are not always an exact measurement of reactivity [73] and values may be affected by the presence of more than one gas [74, 75]. Many definitions of LOT are found

in the literature, such as the temperature needed to attain a significant combustion of fuel, ranging from 10 % [27, 60], 50 % [74-76] , 80 % [77], or even a temperature where the catalyst ignites [11]. A hydrocarbon which gives a lower LOT relative to other hydrocarbons over a particular catalyst is considered more reactive.

Other definition of hydrocarbons reactivity involved a comparison of reaction rate constant at a given oxidation temperature. In this case the higher the rate constant, the more reactive a hydrocarbon is considered to be [61]. Nevertheless, light off temperatures are useful as a measure of combustion reaction activity.

In contrast to hydrogen and methanol, the catalytic combustion of saturated hydrocarbons is significantly more difficult. Hiam et al.[61] reported the activity pattern of $C_4H_{10} > i-C_4H_{10} \sim C_3H_8 > C_2H_6$ over a Pt filament. Moro-oka et al. [78] studied catalytic combustion of saturated and unsaturated hydrocarbons over various metal oxides, where Pt and Pd were found as the most active catalysts. Some experiments on competitive oxidation of hydrocarbons were carried out by the use of mixed hydrocarbons and the activity pattern followed $C_3H_8 > C_2H_4 > C_3H_6 > C_2H_2 > i-C_4H_{10}$. While Hiam et al. observed the absence of any stable intermediate oxidation products, Moro-oka et al. suggested some intermediates may arise due to the breaking of C-C bonds which rapidly equilibrated with gas phase components.

Burning natural gas, gasoline, and fuel oil involves mostly the oxidation of alkanes [79], which can be presented by the following equation



The heat of reaction (2.8) per mole of hydrocarbon increases with the molecular weight of the paraffin, whilst the heat of reaction per g-atom of oxygen is essentially the same [28]. In paraffin molecules, the carbon and hydrogen atoms are bound to other carbon atoms by strong σ -C-C- and σ -C-H bonds. These bonds are slightly polar and the C-H- and C-C- binding energies are rather close, with methane possessing the strongest bond. Moreover, the energy of the C-H bond decreases with the increasing distance between a CH₃ – group and the mentioned bond, therefore, in normal paraffins, C_nH_{2n+1} -H binding energy decreases as the chain is lengthened [28].

The oxidation of methane over platinum catalyst at high temperatures (ca. 1000 °C) exhibits a heterogeneous-homogeneous mechanism [80-83]. The homogeneous steps are caused by a chain reaction in the gas phase and to homogeneous catalysis by partially evaporated platinum [80]. However, at lower temperatures, methane oxidation over Pt, Pt-Rh and Pt-Ir alloys [83], as well as Ag [84] is a heterogeneous process. Apart from noble metals, metal oxides of Co₃O₄, NiO, MnO₂ and PdO exhibit high activity for methane combustion [28, 85].

Methane combustion is practically irreversible and producing carbon dioxide and water as predominant products [28], but Trimm and co-workers [86, 87] have reported partial oxidation products. Working with Pd catalysts (which suffered bulk oxidation under excess oxygen) and temperatures of 280 – 480 °C, a small amount of formaldehyde and traces of hydrogen were detected. Moreover, competitive adsorption between mixed methane-

propane, and methane-formaldehyde/or methane-methanol were evident. The reactivity followed CH_3OH , $\text{HCHO} \gg \text{C}_3\text{H}_8 > \text{CH}_4$. Partial oxidation products are, however, rare, and total oxidation is much more common.

Yao [88] demonstrated that Pt, Pd, and Rh exhibit different kinetic behaviour and activities for the oxidation of individual alkanes. Platinum is generally more active for alkanes except methane, while rhodium is the least active. The higher activity of Pt was attributed to the smaller oxygen coverage on Pt, due to its higher ionisation potential in comparison to Pd and Rh.

For the total oxidation of C_2 - C_8 paraffins, a high activity is exhibited by Pt and Pd [77, 78, 89-95]. The rate of reaction for the oxidation of pentane and heptane is first order while, for the oxidation of isooctane, second order kinetics are observed [91, 95]. The latter is considered difficult to interpret since the participation of two molecules of a complex structure in the rate determining step is doubtful [28].

Light off temperatures (LOT) of n-hexane and its isomers over Pt were ca. 300 °C, with carbon dioxide, water and small amounts of carbon monoxide as products [90]. Reactivities decreased in the order n-hexane, 2,3-dimethyl butane > 2,2-dimethyl butane.

Extensive reviews by Golodets [28] revealed that, apart from Pt and Pd catalyst, there was a similar trend of the activity patterns of metal oxides in catalysing the oxidation of $\text{C}_1 - \text{C}_8$ paraffins. Co_3O_4 , MnO_2 , Cr_2O_3 and NiO exhibited the highest activity in comparison to CuO , Fe_2O_3 , ZnO , TiO_2 , and CeO_2 , whilst V_2O_5 , MoO_3 , WO_3 , Nb_2O_5 , ThO_2 , ZrO_2 and La_2O_3 showed the lowest activity. Moreover, the general trend of paraffins oxidation over metal

oxides involved increasing reactivity as the number of carbon atoms of normal paraffins increased, whilst the reactivity decreased with the degree of branching in the carbon skeletons.

The behaviour of individual hydrocarbons and mixed hydrocarbons with respect to oxidation has been studied for years. Mabilon et al. [76] , in tests with a commercial Pt-Rh catalyst, found that alkynes (in particular acetylene) inhibited the strongest adsorption of all unsaturates and effectively determined the light-off temperature of other compounds.

Patterson et al. [74, 75] investigated the oxidation of 1-hexene, toluene, and benzene over Pt, Pd and Rh catalyst. They found that the reaction behaved differently in mixtures than when they were reacted alone. When the unsaturates were reacted singly in excess of oxygen, the order of hydrocarbon reactivity was benzene > toluene > hexene for Pt, toluene >> benzene-hexene for Pd and hexene >>benzene-toluene for Rh. This phenomenon was due to the substantial influence of the relative strength of adsorption of the reactants on different metals. It is interesting to note that, in the hydrocarbon mixture, isooctane lit-off at 192 °C for Pt, 263 °C for Pd, and 294 °C for Rh respectively: no single isooctane LOT was reported.

Thus, it is clear that the oxidation of light and heavier hydrocarbon mixtures involves the existence of competitive adsorption. As a result, the activity pattern of the oxidation of each compound involved in the mixture may be different from their respective individual species.

By far the largest market for chemical reactors is the vehicle catalytic converter [11]. Attempts have been made to obtain catalysts which exhibit lower light off temperatures, but significant initiation of hydrocarbons combustion was only observed at ca. 200 °C [11, 96, 97]. Supported noble metals [62, 97, 98] and metal oxides [99, 100] have been explored, with the highest activity depending on the support. Overall, noble metals are favoured with Pd preferred for methane combustion [88, 98, 101] and Pt for other hydrocarbons [61, 88, 102]: Pt-based catalysts perform better for methane oxidation in the presence of hydrogen sulfide [62].

In general, catalyst support also plays an important role in determining overall reactivity. The effect of using various precursor Pd salts and different support materials in the preparation of Pd catalysts for CH₄ combustion was investigated. Catalyst activities increased dramatically after heating in a 1% CH₄-air reaction mixture. These activation effects were altered according to the precursor salt and support material used. The activation of SiO₂ samples occurred over short time periods (min-h) while the activation over Al₂O₃ was more prolonged (up to 8 days). Many factors which could be responsible for the activation were investigated and discussed, but none were significant in initiating catalyst activation. Reconstruction of the Pd oxide crystallites was proposed as a cause of catalyst activation. Possible mechanisms for this reconstruction were considered. Only a small fraction of the Pd surface was active for CH₄ combustion [103, 104].

Palladium supported on a moderate acid strength support (silica-alumina) showed the highest catalytic activity for the catalytic combustion of propane [105].

The effects of additives on supported noble metal catalysts for oxidation of light hydrocarbons was studied by Wu et al.[106] using stoichiometric ratios of hydrocarbons to

oxygen. For Pt and Pd catalysts supported on alumina or zirconia, the oxidation of propene were claimed as significantly affected by the addition of NaOH and H₂SO₄. The activity of propene oxidation was promoted by increasing the basicity of the support. This was reflected in the light off over Pt/H₂SO₄/ZrO₂ (260 °C) versus Pt/NaOH/ZrO₂ (190°C) and Pt/H₂SO₄/Al₂O₃ (255 °C) versus Pt/NaOH/Al₂O₃ (180°C). It is interesting to note that the light off of Pt/ZrO₂ was higher than Pt/Al₂O₃ (245 °C versus 220 °C), but this was not sufficiently discussed. Increasing the acidity of the support was beneficial for the oxidation of propane over Pt, but the effect was insignificant for the oxidation of propane over Pd. This was attributed to the difference in reaction mechanism of propane oxidation over Pt and Pd catalysts. The lowest light-off temperatures were 180 °C for propene over Pt/NaOH/Al₂O₃ and 185 °C for propane over Pt/H₂SO₄/ZrO₂.

The reactivity of light hydrocarbons (methane, ethane and propane) over Pt/ δ -Al₂O₃ and Ni/MgO catalysts has been investigated [27, 59, 68, 69, 106]. The Pt catalyst was found to be more active than Ni but, once the Ni was reduced, the reactivities were comparable. The light off temperatures decreased with increasing carbon number and this was in agreement with the general trends observed by Golodets [28] for paraffins. Moreover, the ignition temperatures decreased with increasing fuel/oxygen ratio due to the possibility of indirect partial oxidation. Therefore, light off also reflects the significance of different reaction paths [2].

The attainment of hydrocarbons light off (LOT) was carried out by combusting methanol at ambient over pre-reduced catalysts [69]. As a result, it was required to study the ignition temperature of a mixed hydrocarbon and methanol. By comparing individual LOT of methanol and isooctane over a mixture of methanol and isooctane, Burke [107] concluded that isooctane did not affect the LOT of methanol. Therefore, the LOT of less reactive fuels

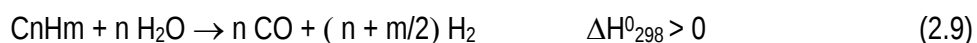
could be achieved by the use of heat produced by earlier combustion of more reactive fuel [2].

The effect of preparation methods on supported noble metal catalysts for oxidation of volatile organic compounds was recently studied by Scire et al. [97]. Au/CeO₂ catalysts prepared by deposition-precipitation route significantly lowered light off temperatures of 2-propanol, methanol and toluene, compared to co-precipitated catalysts. This was attributed to the occurrence of gold nano-particles which were preferentially located on the ceria surface.

Thus, it is obvious that, the reactivity of hydrocarbons combustion is influenced by the interplay among the choice of metal, the type of support and the method of catalyst preparation.

2.5 Catalytic steam reforming of fuels

Catalytic steam reforming is a major process for the conversion of hydrocarbons into hydrogen, carbon oxides and methane, and involves the general stoichiometric equations of [108, 109] :



While reaction (2.9) is known as the reverse of the Fischer-Tropsch synthesis (which takes place below ca. 350 °C [108, 109]), it is considered as an irreversible reaction at higher temperatures provided that $n > 1$. This is in contrast to the water gas shift of reaction (2.10) and methanation reactions (2.11) which are reversible at the temperatures of steam reforming [108, 109].

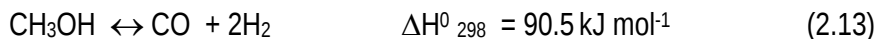
To achieve maximum conversion, the thermodynamics of steam reforming indicates operation at high temperature and low pressure [3]. Metals of group VIII catalyse steam reforming and nickel is more popular for industrial use because of economics [3].

In the context of mobile fuel cells, Burke [107] has discussed methane steam reforming in detail and suggested that methane may not be used as a fuel for automotive applications. However, for stationary fuel cell applications, methane steam reforming is a good candidate to be considered. Consequently, this survey focuses on the use of higher hydrocarbons and alcohols as potential candidates for vehicular fuel cell application.

2.5.1 Steam reforming of alcohols

In the context of fuel processing for fuel cell applications, alcohol fuels such as methanol receive attention worldwide due to the fact that they have the benefits of being almost sulphur-free clean fuels and easier to reform at lower temperatures [9].

The conversion of methanol to hydrogen involves the following reactions [3, 110, 111] :



Reactions (2.12) and (2.10) are steam reforming whilst reaction (2.13) is thermal decomposition. The technology of methanol steam reforming over Cu/Zn/Al is well established and the optimum operating conditions is suggested to be a steam : methanol ratio of 1.5 within a temperature range of 250 – 300 °C [3].

Recent reports involving methanol steam reforming over Pd/ZnO claimed to lower selectivity to CO and to exhibit high activity [112]. Agrell et al. [113] studied suppression of CO formation for the steam reforming of methanol over Cu/ZnO/Al₂O₃ catalyst by shortening the contact time and lowering the reactor temperature in order to suppress the reverse WGS reaction.

Although methanol is suggested as a fuel in the context of on-board hydrogen generation [10, 112-114], computer simulations for the use of more realistic process conditions reveals that methanol is less efficient compared to propane or isooctane [13].

Ethanol, in contrast to fossil fuels, is known as a renewable fuel for the production of hydrogen since it can be derived from bio-mass [115]. Steam reforming of ethanol is thermodynamically feasible and the desired reaction to produce hydrogen and carbon oxides is predominant at ca. 430 – 530 °C and at higher steam : ethanol ratios [116]. Regrettably, only limited experimental efforts have been published probably due to the problem of carbon formation and to the production of undesirable compounds such as methane, acetaldehyde and diethyl ether [117].

Ni/La₂O₃ catalyst or (Ni/La₂O₃)/Al₂O₃ pelletised catalyst exhibits high activity and good stability for steam reforming of biomass-derived ethanol at 300 – 800°C and a steam : ethanol ratio of 3. The product distribution involves hydrogen, carbon oxides, methane, acetaldehyde, ethylene, and ethane [115].

The prevention of coke formation and an increase of hydrogen yields to close to equilibrium was apparently achieved by the use of a two layer fixed - bed reactor. The first bed employed Cu/SiO₂ catalyst to convert ethanol into acetaldehyde at 370°C, followed by production of a hydrogen-rich mixture at 650°C in the second bed over an Ni/MgO catalyst. A steam : ethanol ratio of 8.2 is used for this process [117].

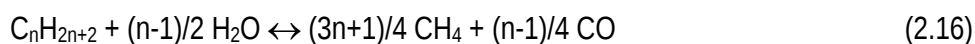
More recently, a hydrogen rich mixture up to 33 % was demonstrated for the steam reforming of ethanol over Ni/Cu catalyst, but CO remained a problem in the context of fuel for fuel cells, and the use of WGS reactors had to be considered [118].

2.5.2 Steam reforming of hydrocarbons

Hydrogen production by steam reforming of light hydrocarbons is a well established industrial process [108, 109, 119, 120] and has been discussed in detail [3, 24, 108, 109, 121-145]. The reaction is endothermic and favoured at high temperatures [108, 109, 119]



Methane production may occur at lower temperatures [2]



The reactions are at equilibrium in industrial application, and the water gas shift reaction is significant to the product distribution



The equilibrium constant, K_p of reaction (2.10) is written [119]

$$\ln K_p = -3.79762 + 4159.54/T \quad (2.17)$$

It is clear that the production of carbon dioxide is favoured at lower temperatures.

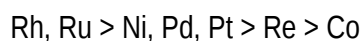
Since steam reforming is carried out at elevated temperatures, coke formation is a major problem [21, 22, 102, 108, 109, 146]. As a result, steam : carbon ratios higher than stoichiometric have to be maintained for promoting carbon gasification. The propensity of carbon formation along with the thermodynamic of carbon production limits in the presence of carbon dioxide and steam has been discussed [24]. Even though kinetic studies predict a slower reaction in comparison to steam reforming [24], carbon dioxide reforming is also possible



A steam:carbon ratio of about 2.5 is suggested as a minimum to avoid coke formation, but this may vary according to the type of hydrocarbons [2].

The susceptibility to carbon formation restricts steam reforming to light hydrocarbons for industrial applications, but the steam reforming of heavy hydrocarbons has been practised [147-149].

An activity pattern of supported metals, either on alumina or magnesia, has been proposed by Rostrup-Nielsen many years ago [121]



Nickel is widely accepted as the most cost-effective catalyst [108, 109, 119, 150], despite the fact that Rh and Ru suppress carbon formation [108, 109].

The choice of support plays an important role in the gasification of coke or of intermediates leading to coke [2, 146]. Magnesia [122] or potassia [119] known to promote carbon gasification by steam. More recently, rare earth oxides, in particular ceria supports, improved catalyst activity and suppressed carbon deposition [21]. Wang and Gorte [151] studied the steam reforming of n-butane over 1 wt% Pd/ceria, 1 wt% Pd/alumina and 15 wt% Ni/silica between 300 and 600 °C, with relatively low steam : carbon ratios (1 and 2). Whilst immediate coking was observed over Ni/silica, the reaction rates on Pd/ceria were stable. However, no comparison was made between 1 wt% Pd/Silica or Ni/ceria under the same reaction conditions. A dual mechanism in which ceria is oxidised by steam and can then supply oxygen to the metal is suggested as the reason of the high activity.

The investigation of steam reforming over Pd/ceria between 350 and 500 °C was extended to light (methane and ethane) and heavy (butane, hexane, 2,4-dimethylhexane, octane, cyclohexane, benzene and toluene) hydrocarbons [152]. While the effect of changing metal from Pd to Pt resulted in slightly different catalytic properties for the reactions, the effect of ceria was significant, with Pd/ceria exhibiting higher rates and selectivities for most reactions compared to Pd/alumina. Regrettably, no hydrogen yields or selectivities were reported due to the inability of the accurate measurement of hydrogen content.

Small amounts of molybdenum dopants (ca. 0.5 wt%) increased resistance to carbon formation for the steam reforming of butane over Ni/ α -Al₂O₃ catalysts. In contrast to ceria dopants, the role of Mo promoter did not increase the gasification rate of deposited carbon, but it reduced the reaction of coke formation. As a result, the amount of coke decreased significantly [150].

Interest in steam reforming of liquid hydrocarbons dates back about four decades [147-149, 153, 154]. In the 1960s, liquid hydrocarbons were introduced for the manufacture of hydrogen and synthesis gas in some areas where natural gas was not available. This resulted from the successful development of catalysts and feedstock desulphurisation technologies [108, 109, 147]. The conversion of hydrocarbons on nickel catalysts is considered to involve an irreversible adsorption of hydrocarbons on any nickel surface in such a way that only C_1 species desorb off the surface [108, 109]. At above 650 °C, higher hydrocarbons pyrolysis may accompany the catalytic conversion [154] and the degree of reactivity follows: higher hydrocarbons > aromatics > methane. Higher hydrocarbons also increase the risk of carbon deposition, which depends on the hydrocarbon type: aromatics are considered as more susceptible than paraffins [3].

One of the earliest studies of the gasoline steam reforming in the context of on-board hydrogen generation was carried out at The Jet Propulsion Laboratory of California Institute of Technology [18]. The system used Indolene gasoline of $(CH_{1.86})_7$ and Diesel fuel grade 2 of $(CH_{1.915})$ at a mass ratio of steam : carbon of ca. 3 – 10 and a reaction temperatures of ca. 500°C – 760°C. A Girdler commercial catalyst (G56 B) which contained 25 % nickel was used. Carbon formation was observed when steam : carbon ratios below 3 was employed. The hydrogen produced by gasoline and diesel fuel steam reforming were ca. 50 % and ca. 35 % respectively. The hydrogen yield of diesel fuel was 20 % lower than with Indolene and this was suggested to occur as a result of increased hydrocarbon output.

Limestone was claimed as a feasible catalyst for the steam reforming of a mixture of 90 % Bunker-C-oil and 10 % of kerosene, using a fluidised bed reactor at 800°C and a steam : carbon ratio of ca. 2 – 4. The hydrogen yield (1 mol of hydrogen produced/mol of carbon consumed) was reportedly similar to a commercial nickel catalyst, but whether results were influenced by cracking reactions was not extensively discussed. The major problem was due to elutriation of fine particles. No prolonged stability test was reported [155].

More recently, Ming et al. [156] observed the steam reforming of liquid hydrocarbon fuels over a proprietary bimetallic compound supported on alumina and doped with (unpublished) oxide having oxygen ion conducting properties. Under standard test conditions (8 g catalyst, 0.28 g min⁻¹ isooctane feed rate, steam : carbon ratio 3.6, 800 °C), a complete conversion of isooctane was achieved and the hydrogen produced was ca. 70 % or very close to their equilibrium calculations. The amount of hydrogen produced is, to a certain extent, dependent on the amount of hydrocarbon fed. Thus, the hydrogen yield and/or selectivity will provide a fairer parameter than product composition if an efficiency comparison to other systems is attempted. When a regular grade gasoline was tested, a comparable hydrogen product to isooctane steam reforming was observed, but by employing much higher steam : carbon ratio (ca. 6.6). Thus, an absence of coke formation was not surprising. A stable performance of isooctane steam reforming was seen about 300 h of operation at 800 °C and S:C ratio of 3.6. The steam reforming of hexadecane (a surrogate of diesel) was also claimed successfully for 73 h of stability test. A better sulphur tolerance was demonstrated for 220 h by adding 100 ppm sulphur in isooctane and a comparison test over 12 wt. % Ni on alumina. Moreover, integrating the reformer with WGS reactors was claimed to reduce CO level to less than 1%.

Thermodynamic calculations for the steam reforming of octane have been carried out by the author, and results presented in Figure 2.1 to 2.2. The process conditions used were more realistic in the context of on-board hydrogen generation as suggested by Springmann et al. [157, 158]. Calculations were performed with the aid of ASPEN by minimising Gibbs free energy. Data used with the package includes physical and thermochemical properties of all species. A Peng-Robinson equation of state was chosen as default value for oil and gas processing model. Calculation were carried out for operating conditions involving steam : carbon ratios of 2 and 3 and pressures of 101.3 kPa and 506.5 kPa. Octane conversion was 100 % in all cases.

In contrast to steam reforming of methane [3, 23], higher hydrocarbon such as octane are more easily reformed. Complete conversion is attained at lower temperatures, irrespective of operating pressures and steam:carbon ratios. The effect of varying pressures and steam:carbon ratios are shown in Figures 2.1 and 2.2.

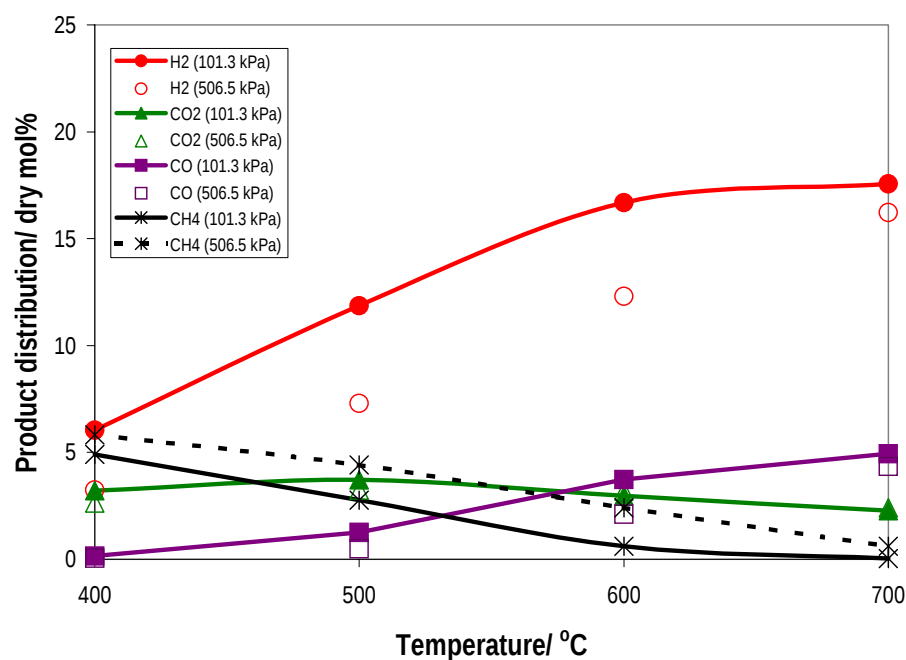


Figure 2.1 Equilibrium product distribution for the steam reforming of octane (steam:carbon ratio 2; inlet octane 1 wet mol %)

As shown in Figure 2.1, hydrogen produced at higher pressure is less than at atmospheric pressure due to the fact that steam reforming is favoured at lower pressure [3]. At 700 °C, the amount of hydrogen produced is essentially the same irrespective of the operating pressure. Consistently, higher methane emerges at elevated pressure (dotted line) due to the difficulty in reforming methane at higher pressure [3, 23]. Methane may be produced by methanation reaction of hydrogen and carbon monoxide as well as carbon dioxide. At above 500 °C, carbon dioxide decreases due to dry reforming reaction. Carbon monoxide increases as the temperature increases due to the reverse water gas shift reaction, which is favoured at higher temperature.

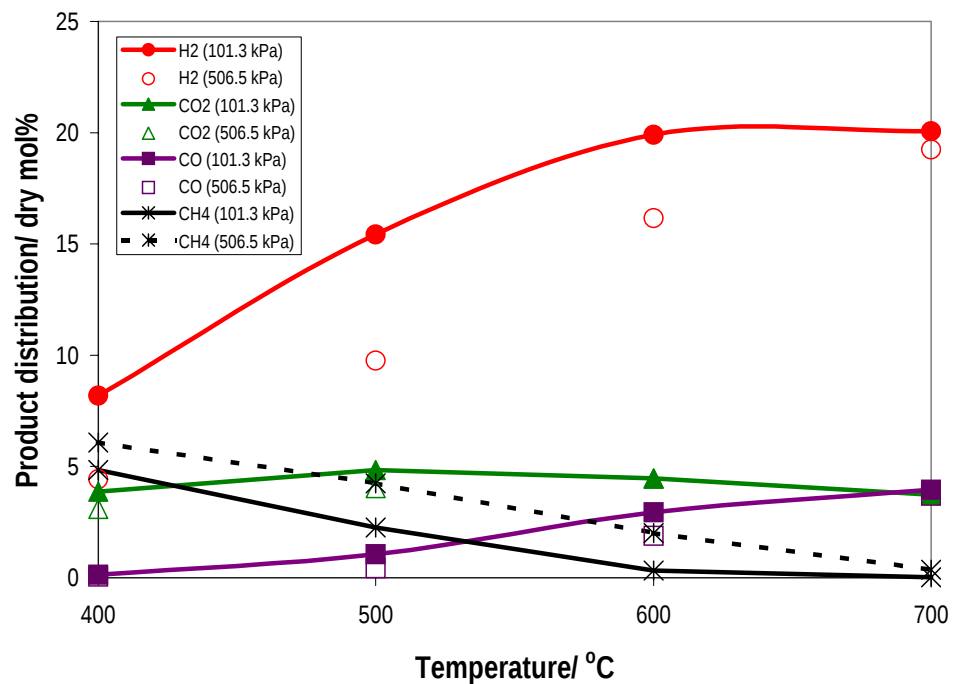


Figure 2.2 Equilibrium product distribution for the steam reforming of octane (steam:carbon ratio 3; inlet octane 1 wet mol %)

When the steam:carbon ratio is increased from 2 to 3 (Figure 2.2), more hydrogen is produced and methane is easier to be reformed. At 600 °C and atmospheric pressure, all methane is essentially used up.

The assessment by thermodynamic analysis clearly predicts that in the context of on-board hydrogen generation, the optimal operating temperature is 600 °C for steam reforming of gasoline. Increasing the temperature does not significantly increase the amount of hydrogen due to the constraint of the reverse water gas shift reaction.

2.5.3 Kinetics of hydrocarbons steam reforming

The kinetics of methane steam reforming have been studied for almost five decades and extensive reviews are available [159]. Much disagreement has been reported with regard to the dependency on steam reaction order, involving positive, zero or negative values depending on the steam partial pressure employed. Eventually, Elnashaie et al. [159] introduced the concept of non-monotonic kinetics based on the kinetic expressions proposed by Xu and Froment [160], which were believed to be the most reliable kinetics on methane steam reforming. It is interesting to note that Xu and Froment observed a positive value of heat of chemisorption of steam and this will be discussed later (Chapter 8).

Even so, there is very little discussion of the steam reforming kinetics for higher hydrocarbons.

2.5.4 Coke formation in hydrocarbon steam reforming

Steam reforming of hydrocarbons involves the risk of carbon formation as the major problem.

Coke is defined as a collective description of various kinds of carbonaceous deposit formed in the reactor [21, 22, 146]. Normally, the hydrogen-rich gas leaves the reformer between 700°C and 950°C, depending on the application [136], and these temperatures may cause catalyst and support sintering and the formation of coke [21, 22, 146].

Coke may be formed by different routes and Rostrup-Nielsen has identified whisker-like carbon, encapsulating carbon, and pyrolytic carbon [108, 109]. Whisker coke is formed at above ca. 450°C by diffusion of carbon through Ni-crystals in such a way that nucleation and whisker growth occur with Ni-crystal at the top of the whisker. Despite the fact that it may not deactivate Ni- surface, coke may break the catalyst down and increase pressure drop significantly. The mechanism of whisker coke from higher (liquid) hydrocarbons involves adsorption of the hydrocarbons on the nickel surface, followed by formation of C₁-species due to successive α -cleavage of the carbon/carbon bonds. These are then step wise dehydrogenated into adsorbed carbon atoms which may dissolve into nickel crystal. Once the carbon concentration is above saturation, then nucleation of a carbon whisker is observed [24]. Dehydrogenation of adsorbed naphtha on nickel catalyst has also been suggested as the rate determining step of coke formation for naphtha steam reforming over nickel catalyst [154].

Encapsulating coke is formed below ca. 500°C due to slow polymerisation of hydrocarbon radicals on the Ni-surface to form an encapsulating film, which may deactivate catalysts progressively. Both whisker and encapsulating coke are catalytic [21].

Pyrolytic coke originates from thermal cracking of hydrocarbons at above ca. 600°C which is then followed by C-precursors deposition on catalysts [3]. Pyrolytic coke will deactivate catalysts and increase pressure drop.

Trimm suggested various methods of coke control [21]. The first technique involved ensemble size control on the nickel surface by adding controlled amounts of sulphur, as has been practised by Haldor Topsoe for their SPARG process [3]. Adding metals dopant to interact with nickel in an attempt to prevent nickel carbide formation was a second option. Small amounts of tin have been found to reduce coking [21]. A small amount of ca. 0.5 wt% Mo doped on to nickel catalyst improved coke resistance for the steam reforming of n-butane [150]. The third method was rare-earth oxides doped on catalyst supports, which favoured coke gasification as reported by Ma et al. [161].

2.6 The autothermal reforming of fuels

Autothermal reforming (ATR) involves the reaction of fuel, oxygen and steam for the production of hydrogen





The combustion of part of the fuel is highly exothermic (reaction 2.19) and provides sufficient heat to drive steam reforming (reaction 2.20) and also produce some water. This is not enough for steam reforming and water gas shift (reaction 2.5), and additional water is required [2, 13, 162-165]. Essentially, the process is a combination of total oxidation and steam reforming of fuels. The reaction products contain a mixture of hydrogen and carbon oxides, with the relative concentration being determined by the water gas shift (reaction 2.5) if thermodynamic equilibrium is attained [166]. Although autothermal reforming is not a new concept (it was used in the early part of the 20th century in many European countries [167] and was well established for the operation of a secondary reformer in ammonia synthesis train [3]), it was Jenkins [168] who first developed a modular stand alone system to convert fuels to hydrogen for on-board vehicular applications.

For transport applications, the system should be able to withstand multiple start-ups/shutdowns, achieve maximum power from cold start in ca. 1 min, responding to changes in the power demand from 10 to 90% in 1 s, and having a power density of 800 W l⁻¹ [169]. Thus, the ability to start the system at ambient temperature is advantageous.

Steam reforming is limited by heat transfer and does not respond quickly to changes in power demand. As a result, when power demand decreases rapidly, the catalyst can overheat, causing sintering which leads to a loss of activity [166]. The load following

limitations of steam reforming can be overcome by autothermal reforming, due to the fact that the heat needed for endothermic reactions is generated in the catalyst bed, thus allowing quicker response to changing power requirements and faster start-up [170].

Modelling studies of autothermal reforming of fuels have recently been carried out [4, 6, 7, 13, 162-166, 171-173]. The theoretical calculation of reforming efficiency (which is correlated with the number of carbon and hydrogen as well as the heat of formation of the fuel) gives the highest value when the process is conducted under thermoneutral conditions ($\Delta H_r = 0$) [6, 7]. Krumpelt et al. [166] proposed the equilibrium calculation for autothermal reforming of isooctane at various oxygen:octane ratios and a water:carbon ratio of unity. There were two extremes: at an oxygen:isooctane ratio of 0, the only reaction occurring was steam reforming and 75.8 % of hydrogen was produced. On the other hand, when the oxygen:isooctane ratio was adjusted to 12.5, complete combustion occurred with a reaction temperature above 2000 °C and no hydrogen was produced. If the ratio of oxygen:isooctane was altered to 2, the reaction was thermoneutral. At ca. 700 °C and an oxygen:isooctane ratio of 4 (O:C = 1), the maximum concentration of hydrogen was 35.5 %. If the reaction temperature was above 700 °C, hydrogen decreased due to a reverse water gas shift reaction. Regrettably, no inlet concentration of isooctane was provided.

Avci et al. [13] studied the conversions of methane, propane, octane and methanol to hydrogen under conditions pertinent to fuel cell operation by a series of computer simulations. Catalytic conversion may be achieved by direct partial oxidation or by a combination of total oxidation and steam reforming. Both systems were simulated, using conversion data and kinetic equations reported in the literature for various catalyst configurations and hydrocarbons. The results showed that, in terms of hydrogen produced

per weight of fuel and water carried, direct partial oxidation of propane or autothermal reforming of octane were the best alternatives. The latter possesses the ease of operation but coke formation may be more of a problem. Methanol, often suggested as a fuel, was much less efficient. Operation of a vehicle using the catalytic conversion system would require fueling by both hydrocarbon and water.

Besides extensive modelling studies, only very limited experimental outcomes were published and mostly for light hydrocarbons and methanol autothermal reforming [59, 69, 106, 111, 166, 174-180].

The most recent studies of the autothermal reforming of methane involved effects of various supports and transition metals.

Takeguchi et al. [180] studied autothermal reforming of methane over supported CaO-CeO₂-ZrO₂ nickel-based catalysts. Significant methane conversions were observed above ca. 500 °C and the activity pattern followed Ni/(CaO)_{0.09}(ZrO₂)_{0.91} > Ni/ZrO₂ > Ni/Al₂O₃. Ceria doped nickel-based catalysts (Ni/CaO-CeO₂-ZrO₂ series) were observed to increase the activity; surprisingly, to give almost the same values of carbon monoxide yields (43.2% versus 41.4 %). The hydrogen yield (8.7% at 550 °C) was lower compared to the results from partial oxidation studies of methane over Ni/(CaO)_{0.09}(ZrO₂)_{0.91} (54.3% at 550 °C) regardless of their different definitions of hydrogen yields between partial oxidation and autothermal reforming. But, no further discussion was attempted.

Using various transition metals, Ayabe et al. [179] reported the activity pattern of Rh > Pd > Ni > Pt > Co for the autothermal reforming of methane, but the activity of Ru was not checked. This pattern was essentially similar to the pattern of steam reforming as proposed by Rostrup-Nielsen [122]. Severe coke formation was observed for the autothermal

reforming of propane over Ni-based catalysts, despite the fact that excess amounts of steam were used. This was attributed to the thermal decomposition of propane to carbon and lower hydrocarbons at the inlet of the catalyst bed. Regrettably, no attempts were made to investigate autothermal reforming over Rh-based catalysts, although the highest activity for the autothermal reforming of methane was observed over this particular metal.

Using the Hot Spot TM reactor, Jenkins and Shutt performed an extensive study of hydrogen generation from various hydrocarbons [168] on a 1% Pt: 3 % chromia:silica catalyst. None of the fuels were able to auto-ignite at ambient. Yields and selectivities were more sensitive to the oxygen:carbon ratio as compared to methanol reforming. A hydrogen selectivity of more than 80 % was achieved at an O:C ratio of 2 by the use of a lead free gasoline. However, results from commercial diesel fuel were erratic.

Fierro [177] studied autothermal reforming of methanol over Cu/ZnO(Al) catalysts prepared from hydrotalcite-like precursors at steam:oxygen:methanol ratios of 1.3:(0.2-0.5):1 and reaction temperatures ranging from 250 to 325 °C. Complete conversion of methanol and zero levels of CO were claimed at ca. 275 °C. Using a commercial Cu/ZnO/Al₂O₃ catalyst, Geissler et al.[111] reported almost complete methanol conversion and 85 % hydrogen yields at ca. 300 °C. Velu et al. [174] demonstrated almost 100 % conversion of methanol and nearly 80 % hydrogen selectivity over a Cu/Zn/Al/Zr at ca. 230 °C under a steam:methanol ratio of 1.6 and an oxygen to methanol ratio of 0.25. Carbon monoxide level was claimed to be ca. 1400 ppm. Shen and Song [176] compared the effect of preparation method on the performance of Cu/Zn-based catalysts for autothermal reforming at 230 °C, under oxygen:methanol and steam/methanol ratios of 0.47 and 1.43

respectively. A sample prepared by co-precipitation was found as the best catalyst and a CO level of ca. 0.05 % was claimed.

A bimetallic Ni-Pd/Al₂O₃ catalyst exhibited higher activity and selectivity compared to Ni/Al₂O₃ or Pd/Al₂O₃ for the partial oxidation and steam reforming of n-octane as a model for gasoline [178]. Better stability (100 h running test) was also reported for the bimetallic catalyst, but care should be taken in interpreting the stability results since the amount of air and the steam:carbon ratio were ca. doubled in comparison to single metal observations. For Pt or Pd on Al₂O₃, an air:octane ratio of ca. 5 and a steam:carbon ratio of 3 were used while, for the bimetallic sample, an air:octane ratio of 9.5 and a steam:carbon ratio of 5 were employed. This in turn, increased the conversion of hydrocarbon from ca. 50% to ca. 100%. Therefore, little or no carbon deposition was not surprising.

Moon et al. [181] suggested an O:C ratio of more than 0.6 and steam:carbon ratio of 1.5 to 2.0 for the ATR of isooctane, toluene, and gasoline over a commercial methane steam reforming catalyst. Carbon formation was reported below 620 °C and below 640 °C for the ATR of isooctane and toluene respectively. It was also found that the coke deposition on the surface of catalysts was promoted by sulphur in fuels. Moreover, Moon et al. [182] extended their studies for a combined autothermal reforming and water gas shift reaction of isooctane in the absence and presence of sulphur, and of reformulated naphtha over commercial naphtha reforming, Fe₃O₄-Cr₂O₃ and CuO/ZnO/Al₂O₃ catalysts. Working with O:C of 1 and S:C of 3, an overall hydrogen production of ca. 50% was observed and the level of CO was reduced to less than 3000 ppm. Despite the fact that the commercial reforming catalyst was prone to be poisoned by sulphur (reflected by increased CO₂ and CH₄ products), no carbon formation at 700 °C was claimed - but no evidence of decoking

was provided. At higher space velocities (above 17000 h⁻¹), hydrogen production decreased significantly but the reasons was not discussed.

In contrast to Jenkins and Shutt, Moon et al. did not report hydrogen yield and/ or selectivity, and a process efficiency comparison was not possible. Further more, since the actual amount of hydrocarbon fed was not provided, estimates of their hydrogen yield/selectivity by back calculation based on the reported hydrogen product could not be carried out.

Various transition metals supported on doped ceria has been reported as having excellent activity for the autothermal reforming of isooctane between 500 and 800 °C with high fuel conversion and high hydrogen selectivity, but reasons were not extensively discussed. All metals investigated (Ru, Pd, Pt, Ag, Ni, Co, Cu and Fe) exhibited conversions of > 95 % at temperatures above 600 °C except Ag (reasons unknown). At below ca. 600 °C, conversions decreased more rapidly for the first row transition metals (Ni and Co) than for the second row (Ru), and third row (Pt,Pd) transition metals. The second and third row transition metals exhibited higher hydrogen selectivities (ca. above 60%) than the first row transition metals at ca. above 650 °C. At temperatures below 650 °C, the hydrogen selectivities decreased to less than 50 % for all metals, except for Ni and Ru [166]. No details of catalysts preparation were reported. In contrast to commercial steam reforming catalysts [182], a Pt/CeO₂ catalyst was claimed as more sulphur tolerance.

The reformed gas outlet of a fuel processor contains significant amounts of CO, despite the fact that a combined autothermal reforming and water gas shift reaction is employed [2].

The CO tends to poison fuel cells. More recently, significant reduction of CO by selective oxidation was observed by Tanaka et al. [183]. Working with a typical reformed gas (75% H₂, 0.2% CO, 0.2% O₂ and He as balance) over K-Rh/SiO₂ and K-Rh/USY-zeolite at 130 °C, a CO level reduction to less than 10 ppm was reported. The role of potassium dopant was attributed to the enhancement of Rh dispersion (over Rh/SiO₂) and the turn over frequency (over Rh/USY-zeolite), but the change in role of potassium dopant between silica and zeolite supports was not clear.

2.7 Conclusion

In the context of non-stationary hydrogen generation for PEMFC, either partial oxidation employing Rh-based catalysts or autothermal reforming of fuels over composite catalysts may be considered. However, autothermal reforming of liquid hydrocarbons seems to be the most promising option for the hydrogen production on-board vehicles. Part of the fuel can be combusted to produce sufficient heat for driving the steam reforming of unburnt hydrocarbon. Platinum based catalyst was considered as the best active metal for fuel combustion, whilst nickel based catalyst was a preferred choice for steam reforming of the remaining hydrocarbon. The optimum process conditions involved O : C ratios of 0.5 to 1.0 coupled with S : C ratios of 1 to 3 at temperature ranges within 500 – 700 °C. Moreover, autothermal reforming could be initiated at ambient temperature. The problem of using liquid hydrocarbons may rest with the sulphur content in the hydrocarbons. However, recent progress in deep desulphurisation of gasoline over a transition metal-based adsorbent [184, 185] and newly developed naphtha steam reforming catalysts [3] may be

the solution. Carbon monoxide produced by ATR may poison the fuel cell electrodes, and selective oxidation for carbon monoxide has to be coupled in the ATR reformer [2].

2.8 *Project objectives*

The literature survey revealed that hydrogen from the conversion of gasoline is the most suitable fuel for fuel cell in the context of on-board vehicular applications. Moreover, combinations of total oxidation and steam reforming of gasoline is considered as one of the best process.

Previous studies have confirmed the viability of autothermal reforming of methanol and light hydrocarbons. Very limited publications of autothermal reforming of higher hydrocarbons have also indicated that such a process was feasible.

As a result, the present work is dedicated to study the possibility of applying the same concept to convert artificial gasoline (as a model for gasoline) to hydrogen. Investigation is focused on

1. Study of partial oxidation of isooctane over Rh based catalysts
2. Study of total and partial oxidation of artificial gasoline (cyclohexane, 1-hexene, isooctane, octane and toluene) over Pt/CeO₂, Pt/NiO-MgO and NiO/MgO catalysts
3. Study of steam reforming of artificial gasoline over NiO/MgO catalyst

4. Measurement of the kinetics of steam reforming for artificial gasoline over NiO/MgO catalysts
5. Testing of autothermal reforming for artificial gasoline

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Chapter 3 Experimental methods

3.1 Materials

3.1.1 Gases

The bulk gases used in this study were supplied by Linde, Commonwealth Industrial Gases (CIG) Ltd. and BOC, Australia. Scotty Mix gases were obtained for GC calibration which were supplied by Alltech. Gas purity and area of application are reported in Table 3.1.

Table 3.1 Gas specification

Gas	Specification	Use	Supplier
Air	High purity	Carrier gas	Linde
Argon	High purity, 99.99 %	Carrier and diluent gas	Linde
CH ₄ in He	2.08 % $\pm$ 0.08 %	Calibration gas	BOC
CO ₂	High purity, 99.9%	Reactant	CIG
CO ₂ /CO/Ar	7.14 % CO ₂ / 5.89 % CO	Calibration gas	BOC
H ₂	High purity, 99.99%	Carrier and reducing gas	Linde
H ₂ in N ₂	4.99 % $\pm$ 0.01 %	Calibration and reducing gas	BOC
H ₂ in Ar	9.86 % $\pm$ 0.14 %	Calibration gas	BOC
He	High purity, 99.99 %	Carrier gas	Linde
N ₂	High purity, 99.99 %	Carrier and dilution gas	Linde
O ₂	High purity, 99.99 %	Reactant	BOC
Scotty Mix 215	1000 ppm of C ₂ H ₄ , C ₃ H ₆ , C ₄ H ₈ , C ₅ H ₁₀ , C ₆ H ₁₂ , and N ₂ as the balance	Calibration gas	Alltech
Scotty Mix 216	(accuracy $\pm$ 5%) 1 % of CO ₂ , CO, C ₂ H ₂ , C ₂ H ₆ , C ₂ H ₄ , CH ₄ , and N ₂ as the balance	Calibration gas	Alltech
Scotty Mix 218	(accuracy $\pm$ 5%) 1 % of CH ₄ , O ₂ , CO ₂ , CO, H ₂ , and N ₂ as the balance (accuracy $\pm$ 5 %)	Calibration gas	Alltech

3.1.2 Chemicals

All chemicals employed in this study were supplied by Sigma-Aldrich, except for $\gamma\text{-Al}_2\text{O}_3$ for catalyst preparation and bed diluent precursor which was supplied by Norton. Cyclohexane was supplied by BDH, and ethanol supplied by CSR of Australia. Rhodium and platinum salts were kindly provided by Johnson-Matthey. The details are summarised in Table 3.2.

Table 3.2 Chemicals specification

Chemicals	Specification	Use
Ethanol	Technical grade	Solvent for catalyst preparation
Isooctane	99 %	Reactant
Octane	99 and 98 %	Reactant
Cyclohexane	99 %	Reactant
1-Hexene	97 %	Reactant
Toluene	99 %	Reactant
$\gamma\text{-Al}_2\text{O}_3$	High purity	Catalyst preparation/diluent precursor
Cerium nitrate	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99% / La-1 %	Catalyst preparation
Cerium nitrate	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, > 99%	Catalyst preparation
Nickel acetate	$(\text{CH}_3\text{CO}_2)_2\text{Ni} \cdot 4\text{H}_2\text{O}$, 98%	Catalyst preparation
Nickel nitrate	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, > 97%	Catalyst preparation
Aluminum tri-sec.butoxide	97 %	Catalyst preparation
$(\text{NH}_3)_4\text{PtCl}_2$	32 g/L Pt	Catalyst preparation
$\text{Rh}(\text{NO}_3)_3$	32 g/L Rh	Catalyst preparation
Yttrium nitrate	$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, >99 %	Catalyst preparation
Zirconyl nitrate	$\text{ZrO}(\text{NO}_3)_2 \cdot x \text{H}_2\text{O}$, white	Catalyst preparation

3.2 Catalyst preparation

All catalysts, except a nickel commercial catalyst for naphtha steam reforming, were prepared in the laboratory by the use of various methods. The preparation techniques were described in Chapter 4.

3.3 Catalyst pretreatment

3.3.1 Partial oxidation of artificial gasoline

In order to activate rhodium based catalysts, a sequential reduction program was applied by the use of modified Ma technique [1]. About 40 ml min⁻¹ of argon was passed over the loaded catalyst for 10 min at ambient temperature to purge oxygen. The choice of argon was a matter of convenience since the experimental rig was prepared for Argon as a diluent. The inert purge gas was then replaced by a mixture of calibration gas of 5% H₂/N₂ at ca. 50 ml min⁻¹. The catalyst bed was then heated to 150 °C at a heating rate of 10 min⁻¹ and held for 20 min to evaporate moisture. The solid was then heated to 300 °C at a ramping rate of 5 °C min⁻¹ and held for 30 min to release the structural water in the catalysts. Finally, the temperature was increased to the calcination temperature of catalysts (600 °C, 2 °C min⁻¹) and held for 4 h. This complicated reduction program was a compromise to avoid premature sintering due to excessive heat increases and steam evolved during the reduction period. No pretreatment were carried out for platinum based

catalyst beyond the procedures described in Chapter 4, since this was the normal operating condition for the catalyst in real life.

3.3.2 Steam reforming and autothermal reforming of artificial gasoline

Steam reforming and autothermal reforming was carried out using two catalysts – the nickel based system and the platinum based system described in Section 3.5.2 and Section 3.5.3. The activation procedure for nickel and platinum based catalysts was the same as described in Section 3.3.1.

In the autothermal experiments, both catalysts were loaded in the same reactor and were reduced in-situ using the procedure described in Section 3.5.2. The inert purge gas was N₂ and the reducing mixture was 20 % H₂/N₂ at 100 ml min⁻¹, prepared by metering pure H₂ and N₂ with the aid of two Brooks mass flow controllers (model 5850 E).

3.4 *Experimental apparatus*

3.4.1 The reactor

All experiments were carried out using a tubular fixed bed reactor which was made of stainless steel tube (40 mm length x 10 mm inside diameter). A thermocouple was normally inserted in the centre of catalyst bed, except for autothermal reforming studies; In this case temperature measurements were carried out using a sliding thermocouple which could be moved inside a central well in the reactor. This allowed measurement of the axial temperature distribution along the two beds of catalyst.

The catalyst was loaded in the constant temperature zone in the reactor where the reactor contained two catalysts, the two beds were separated using a small wad of quartz wool. The loading sequences are shown in Figure 3.1.

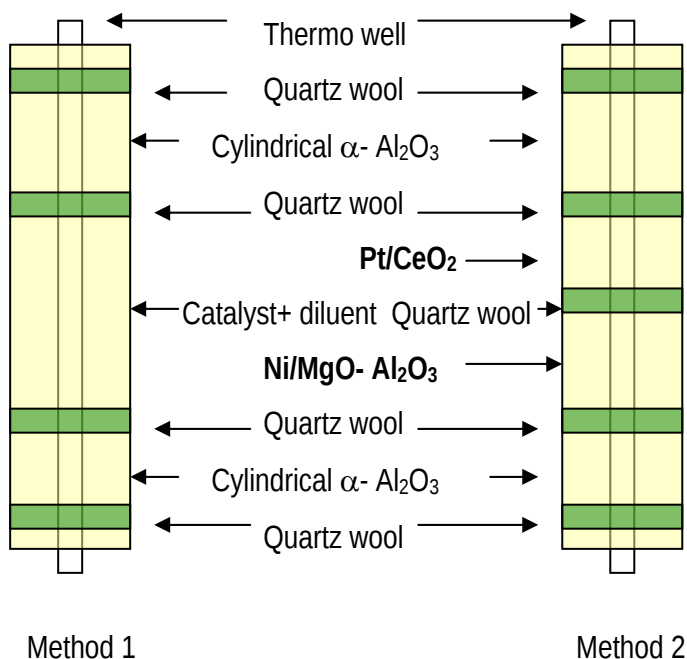


Figure 3.1 Catalyst packing arrangement

3.4.2 Control of temperature for the experimental rig

A cylindrical furnace powered by electricity was used to supply heat to the reactor. The controlling thermocouple was located either in the catalyst bed or between the furnace and the reactor tube. When the latter method was applied, a second thermocouple was inserted in the thermo well in the centre of the reactor in order to monitor the catalyst bed temperature. A mixture of alumina particles and kaowool were used to fill the gap between

the furnace and the reactor in order to obtain a better heating efficiency. All temperature controllers were supplied by Shinko.

Initially, only a Variac was used to supply the power required for the pre-heater, but the pre-heater temperature fluctuated to ca. 300 – 400 °C, which fragmented the hydrocarbons fed to the system. Carbon deposited in the pre-heater tube and blocked the water supply. To control the temperature, a thermocouple (connected to a Shinko temperature controller) was inserted in the centre of pre-heater and the output of a Shinko temperature controller was cascaded to a Variac which was used as a power supply to the pre-heater: the pre-heater temperature was successfully maintained by this method at 200 ± 1 °C. This operating temperature is a compromise between the heat needed to produce steam and the need of avoiding unwanted cracking of hydrocarbons.

The heating lines were controlled at ca. 70 °C by the use of two shielded small transformers. The first transformer was used to supply power to the second transformer whilst the latter supplied power to the heating lines.

3.4.3 The rig configuration

Figure 3.2 shows the simplified diagram of the experimental apparatus for the studies of partial oxidation and/ or steam reforming of gasoline-like hydrocarbons. The flow rates of gas-phase feed were metered by Brooks 5850 E mass flow controllers having the operational flow range of approximately 5 – 200 mL min⁻¹ for lower flow and 10 – 1000 mL

min⁻¹ for high flow. These were calibrated using a soap-film bubble meter within the error of measurement of 0.5 – 1 %. The calibration was carried out under the same conditions as those for relevant to the experimental runs.

The liquid hydrocarbons were picked up by inert carrier gas (either argon or nitrogen) from the first and/ or second saturators (Dreschel bottles which were loaded with mixtures of glass spiral rings, Raschig rings and beads), whilst the third saturator, filled with glass beads, was used as a stabiliser. All saturators were mounted in the Julabo E (hot) and F (cold) 34 water bath which could be controlled at certain temperatures depending on the amount of hydrocarbons to be picked up. Water was pumped by an ISCO 260 D stainless steel syringe pump having a maximum capacity of 260 mL and maximum pressure rating of 20 MPa to the pre-heater (operated at 200 ± 1 °C) before being mixed with reactant gases. All feeds were then brought to the reactor or by passed for the analysis of feed compositions.

A fourth vessel was mounted in the water bath and dedicated as the first water trap. Prior to the analysis of the feed stock and dry gas products, the outlet streams from the reactor passed through this vessel and were sent to a quartz drying tube (150 mm length and 10 mm inside diameter) packed with ca. 5 g of indicating drierite in order to trap the remaining moisture content. Whilst the measurement of flow rates were required, the drierite was by passed and the stream was passed on to two condensers operated at ca. 0 °C by suspending them in ice. By the use of drierite, the water was successfully trapped whilst the condensation of hydrocarbons were prevented.

3.4.4 Product and reactant analysis

For the study of the partial oxidation of isooctane over rhodium based catalyst, a Balzers Thermostar quadrupole Mass Spectrometer (MS) was used to detect all species at inlet and outlet of the reactor.

This particular analyser separates components based on their mass to charge ratios (m/e ratios). Each species has a characteristic spectrum of m/e ratios. Gases enter an evacuated chamber and, under the influence of an electromagnetic field, are separated, resolved onto a detection plate and the resultant electrical signals are amplified. These amplified analogue signals are converted to digital signals by A/D converters contained within the MS before being recorded by a Personal Computer [2].

When an MS was operated, no water traps were used, due to the fact that all compounds including water could be detected by this instrument.

For the study of partial oxidation and or steam reforming of gasoline-like hydrocarbons over platinum and/ or nickel based catalysts, the analysis of product and reactant was conducted using three on-line gas chromatographs operated in parallel by using a four-way switching valve driven by compressed air.

The first GC (GC1) was a Shimadzu 8A type equipped with a TCD detector and a 1.8 m length ($\frac{1}{4}$ inch OD) CTR-1 packed-column. Helium was used as the carrier gas with a flow rate of 40 mL min^{-1} STP. The column temperature was maintained at 40°C and the injector/detector temperature was controlled at 120°C . This GC analysed carbon dioxide, ethylene, ethane, oxygen, nitrogen, methane, and carbon monoxide.

A Shimadzu 8A (GC2) fitted with an FID detector and a 3 m length (1/8 inch OD) Chromosorb-WH/OV-101 packed-column was dedicated to analyse hydrocarbons higher than C₂ (ethylene or ethane). Nitrogen was used as the carrier gas with a flow rate of 50 mL min⁻¹ STP. Hydrogen and Air pressures were kept at 70 and 50 kPa respectively for normal operation and at 20 and 90 kPa for initial start up. The column temperature was programmed from 40 to 120 °C at 3 °C min⁻¹ whilst the injector temperature was kept at 150 °C.

The last GC (GC3) was a Shimadzu 8A fitted with a TCD detector and a Molecular Sieve 13 X packed-column dedicated to analyse hydrogen. Argon was used as the carrier gas with a flow rate of 40 mL min⁻¹. The column temperature was kept at 40 °C whilst the injector/detector temperature was maintained at 60 °C.

Three Shimadzu Chromatopac C-R6A integrators were used to determine peak areas. For the first two weeks, the columns used for TCDs were regenerated regularly and calibrated by standard gas on a daily basis, but the error of measurement was found to be within 3 % even after six months. Therefore it was decided to calibrate the GC occasionally.

Calibration of the liquid hydrocarbons were carried out by the total oxidation of hydrocarbons over a platinum based catalyst. The oxygen used was twice as much as that required to oxidise hydrocarbons into carbon dioxide and water. A known volume of the liquid hydrocarbon was placed in the first saturator which was one third-filled with mixtures of glass packings, immersed in a Julabo waterbath maintained at 20 °C. Nitrogen carrier

gas was bubbled through the saturator at a relatively low flow rate (50 mL min⁻¹) to provide a reasonably long contact time. Prior trials indicated that 50 mL min⁻¹ nitrogen flow was sufficiently low to allow the gas phase partial pressure of each species to attain the level given by Raoult's law [3]

$$P_i = P^0 X_i$$

where

P_i = partial pressure of component i in the gas phase

X_i = mole fraction of component i in the liquid phase

P^0 = vapour pressure of component i at 20 °C.

In order to calculate the amount of required oxygen for the complete combustion of a certain amount of hydrocarbon, an initial estimate of vapour pressure of component i (P^0) was made by employing the Antoine equation [4]. The exact amount of combusted hydrocarbon was then calculated based on the carbon balance (i.e. the amount of carbon in vapourised hydrocarbon corresponded to a peak area measured by FID = the amount of carbon in CO₂ product) .

Whilst nitrogen was used as a tie gas for all species detected by TCDs (GC1 and GC3), the amount of hydrocarbon measured by FID (GC2) was calibrated directly. Initially methane was tried as a tie gas for all GCs but it failed, due to the fact that the chromatograph could not distinguish hydrogen, methane or ethylene/ethane. For a similar reason, a normalised multi point calibration techniques for determining response factors [3] was unable to be applied. As a result, the response factor was defined as:

$$R_i = M_i / A_i \tag{3.1}$$

Where R_i is the response factor of i^{th} species, in mol %/peak area;

M_i is the molar percentage of i^{th} species, in mol %;

A_i is the peak area measured by GC.

Table 3.3 lists the setting values of GCs and integrators, while Table 3.4 shows typical retention times and response factors for various species.

Table 3.3 GCs and integrators setting

Item	1	2	3
GC setting			
Column temperature, °C	40	40 – 120 (3°C min ⁻¹)	40
Inj./det. temperature, °C	120	150	60
Current, m.A.	120	-	80
Range	-	10 ²	-
Attenuation	1	32	16
Integrator setting			
Width	5	5	5
Drift	0	0	0
T.DBL.	0	1000	0
Attenuation	0	5	10
Slope	41.2803	267.36	103.682
Min. area	10	10	10
Stop time, min	15	20	15

Table 3.4 Gas chromatograph retention times and response factors for various species

GC	Species	Retention time, min	Response factor*), mol%/peak area
GC1	Carbon dioxide	1.08	1.75×10^{-4}
	Acetylene	1.57	1.80×10^{-4}
	Ethane	2.10	1.37×10^{-4}
	Oxygen	2.40	1.62×10^{-4}
	Nitrogen	3.20	1.60×10^{-4}
	Methane	5.22	1.72×10^{-4}
	Carbon monoxide	6.53	1.63×10^{-4}
GC2	Propylene	0.51	1.64×10^{-5}
	1-Butene	0.65	2.56×10^{-6}
	1-Pentene	1.00	2.05×10^{-6}
	1-Hexene	1.89	1.69×10^{-6}
	Cyclohexane	2.89	1.47×10^{-6}
	Isooctane	3.61	1.36×10^{-6}
	Toluene	6.52	1.48×10^{-6}
	Octane	7.62	1.36×10^{-6}
GC3	Hydrogen	0.57	7.95×10^{-6}
	Nitrogen	0.73	9.29×10^{-5}
	Methane	1.04	1.25×10^{-4}
	Carbon monoxide	1.16	3.74×10^{-5}

*) error of measurement of peak areas $\pm 0.5 \%$

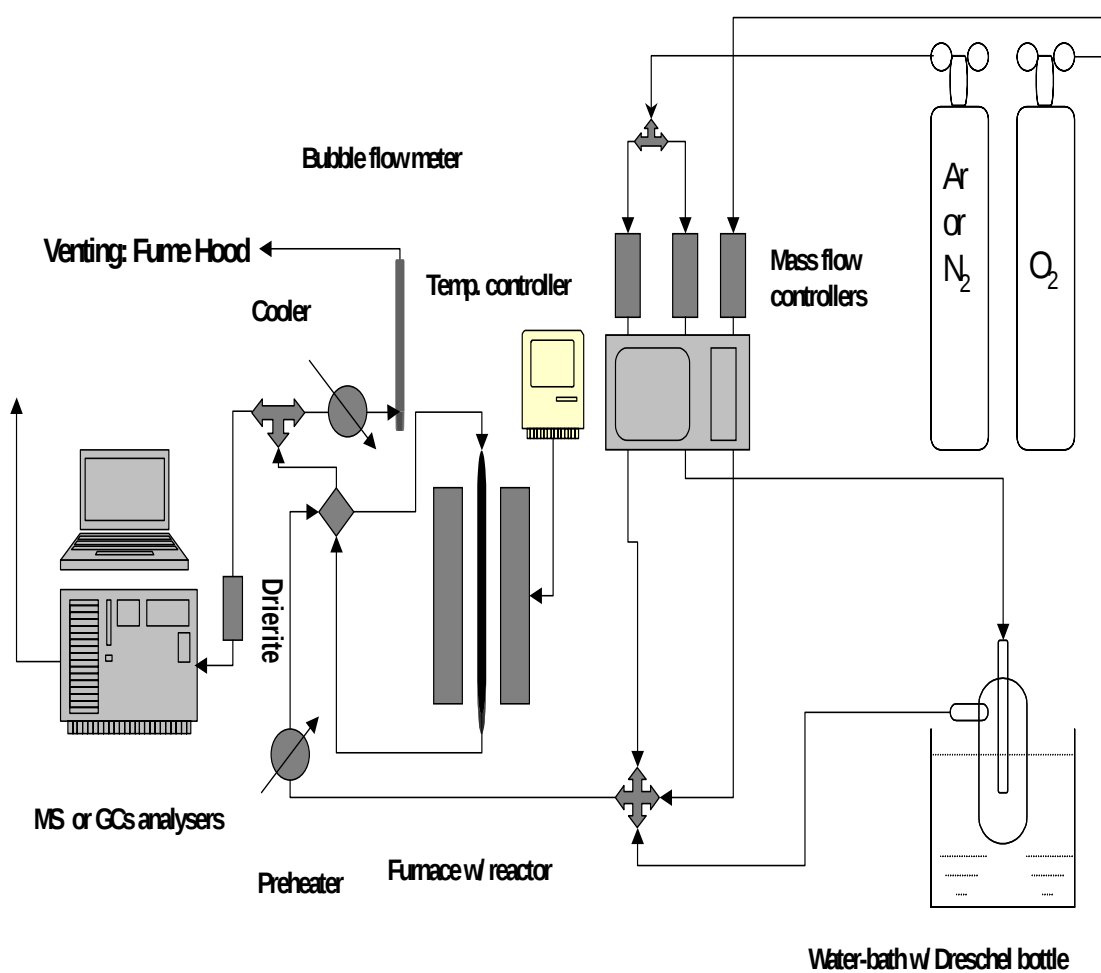


Figure 3.2 A simplified diagram of the experimental rig

3.5 *Experimental procedures*

3.5.1 Oxidation of gasoline-like hydrocarbons

The general procedures described below involved partial oxidation, steam reforming and autothermal reforming of gasoline-like hydrocarbons. More detailed procedures of each experiment is provided in its respective chapter.

For the partial oxidation of isooctane over rhodium based catalysts, a certain amount of catalyst diluted with α -Al₂O₃ powder of the same particle size was loaded into the reactor using a catalyst : diluent ratio = 1 : 9 by weight and reduced in situ using the method described in Section 3.3.1. Following the catalyst reduction, argon as a carrier gas, oxygen and argon as a diluent gas were metered by mass flow controllers individually and then mixed before passing to the reactor. The temperature of the catalyst bed was carefully adjusted and the total pressure in the reactor was essentially one atmosphere. Isooctane was supplied from the saturator. The Julabo water bath temperature was kept at 20±0.4 °C as a compromise between winter and summer seasons so as to avoid any condensation within uninsulated tubings. The concentration of isooctane was kept at 1 % mol which was below the lower level of explosion limit [5] and also as suggested by Mabilon et al. [6], as well as within the range of car exhaust emissions as prescribed by Schmidt [7]. This was done by controlling argon flow rates. Similarly, the molar ratio of isooctane to oxygen was kept constant and expressed as C : O ratio of 1 : 1.56 by controlling argon and oxygen flow rates. The calculation for the establishment of C : O ratio is reported in Appendix i. The diluent gas was changed respectively during the adjustment of operating conditions in

order to keep a constant gas velocity through the catalyst bed. The total dry gas flow rate was measured by a soap-film bubble meter and exit gases were analysed on-line by a Mass Spectrometer.

For the oxidation of all hydrocarbons (either individually or in an artificially mixed gasoline) over platinum, nickel and platinum/nickel based catalysts, a similar catalyst loading technique was applied but no catalyst reduction was carried out. Instead of argon, nitrogen was used as a carrier and a diluent gas. The various C : O ratios were controlled by manipulating nitrogen and oxygen flow rates whilst keeping the water bath temperature similar to the above. The total dry gas flow rate was measured by a soap-film bubble meter and the exit gases were analysed on-line by three gas chromatographs (Section 3.4.4) simultaneously.

3.5.2 Steam reforming of artificial gasoline

Studies for steam reforming of gasoline-like hydrocarbons over nickel based catalysts were carried out using the same reactor as for oxidation experiments. Attention was focused on the insulation of the reaction system to minimise heat loss, and on the provision of better heat transfer medium between the reactor and heating furnace, due to the severity of the endothermic reaction. To do so, the gap between the reactor and the furnace was filled with mixture of Kaowool and cylindrical γ - Al_2O_3 (3-5 mm length x 1.5 mm diameter). The catalyst loading technique was exactly the same as for oxidation experiments.

Prior to use, the catalyst was reduced in-situ using 100 mL min⁻¹ of 20 % hydrogen in nitrogen. A flow of 80 mL min⁻¹ of nitrogen was first introduced to the catalyst bed for ten minutes at room temperature in order to remove any oxygen trapped in the system. About 20 mL min⁻¹ of hydrogen were then added to the system. The next heating sequences followed the procedures described in Section 3.3.1. The catalyst bed temperature was then naturally allowed to cool down under the continuous supply of hydrogen/nitrogen in order to avoid re-oxidising the catalyst. After reduction, the catalyst bed temperature was adjusted to at least 150 °C with a flow of hydrogen/nitrogen mixture passing through the bed. The desired amount of hydrocarbons and steam were then fed to the reaction system by replacing hydrogen/nitrogen mixture. The steam to carbon ratios were maintained to give at least 3 moles of steam per atom carbon in order to prevent carbon deposition. The temperature was carefully set to the desired value, followed by the measurement of conversion and reaction rates under various process conditions.

3.5.3 Autothermal reforming of artificial gasoline

The simultaneous partial oxidation and steam reforming of gasoline-like hydrocarbons was carried out using a *pseudo* adiabatic reactor exactly the same as was employed in the steam reforming experiments. The reactor was charged with Pt/CeO₂ catalyst in the top bed, followed by the NiO/MgO-Al₂O₃ bed. Prior to use, all catalysts were reduced in-situ according to the method described in Section 3.5.2. After pre-treatment, the reactor was cooled to room temperature under the flow of hydrogen/nitrogen mixture. Two monitoring

thermocouples were used. One thermocouple was inserted in the thermo well mounted in the reactor centre to monitor the axial temperature distribution in the catalyst beds, and the other was inserted in the filling materials between outer reactor and inner furnace walls.

To attain the required temperature for driving steam reforming, sufficient hydrocarbon should be supplied to the reaction system, to be burnt with the required amount of oxygen. Therefore, the Julabo water bath temperature was raised to either 50 or 75 °C depending on the maximum bed temperature to be attained. By manipulating the start-up procedures, no initiation using either hydrogen/oxygen or methanol/oxygen mixtures was required. The isooctane picked up by nitrogen was admitted to the reactor for about 1 minute, and followed by the introduction of required amount of oxygen in two steps. The oxidation occurred spontaneously and the catalyst beds temperature rose dramatically until the maximum reactor temperature was achieved. Reversing the order of start-up sequences (i.e. oxygen first, followed by isooctane) would deactivate the catalysts instantaneously and no activity was observed.

A calculated amount of water was then pumped to the reactor. After 30 minutes, the product composition was measured at regular intervals. The steady state was deemed to be achieved when the outlet composition was constant within ± 5 %. No optimum operating conditions were attempted due to safety reason (i.e. inlet hydrocarbons should be kept at 10 % in oxygen/nitrogen environment similar to air composition).

3.6 References

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Chapter 4 Catalysts preparation and characterisation

4.1 Introduction

This section will focus on preparing and characterising well dispersed oxides for catalysts supports by sol-gel methods followed by loading selected metal on to the supports. In particular :

1. To develop sol-gel methods for the preparation of cerium, cerium-zirconium, cerium -yttrium, and cerium-zirconium-yttrium oxides.
2. To investigate surface area stability towards various calcination temperatures of mixed oxides supports
3. To prepare nickel, platinum and rhodium oxide catalysts

4.2 Literature review

4.2.1 Overview of supported catalysts preparation methods

The following discussion is categorised into non-solgel route and sol-gel techniques as described in the literature.

In the context of first category, Geus [1] provides a comprehensive review and divides the preparation procedures into two major groups namely (i) The active precursor loading on to a separately produced support. This involves adsorption, impregnation and drying, as well as precipitation techniques, (ii) Selective removal of one or more components from solids possessing small specific surface area which includes Raney metals, mixed oxalates, and co-precipitates. However in this particular project, attention is focused on the first group since, according to Geus, it has the advantage of adapting support properties to the catalytic process .

An active precursor adsorption from liquids is well suited to the preparation of precious metal catalyst which uses low metal loading. The amount of metal which can be loaded by adsorption is limited due to the fact that multilayer adsorption is rarely observed. Moreover, metal distribution depends on the adsorption sites density of the support which is affected by the metal solution pH. As a result, low metal loading on a support with high adsorption sites density may cause non-homogeneous metal precursor distribution [1, 2].

The objective of impregnation and subsequent drying is to break-up the metal precursor solution into small discontinuous elements present in the support pores while evaporating the solvent gradually [3]. Two impregnation techniques are known, the first of which is incipient wetness, usually applied to pelletised supports. In this case the amount of metal solution added is just enough to fill the pore volume. Secondly, wet impregnation, which is normally used for powdered supports. Since wet impregnation involves larger volumes of metal solution, continuous stirring should be undertaken while the drying operation is in

progress. Higher metal loading may be achieved, but the desired uniform distribution is rarely obtained.

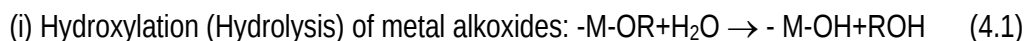
The precipitation of active metal is carried out in the presence of a suspended support. The resulting solid is then filtered, dried, and shaped into pellets followed by calcination. The advantages of precipitation are based on the fact that precipitation is faster than drying, but active metal distribution is worse compared to the impregnation and drying route [1].

Co-precipitation procedure is one of the selective routes widely used in industrial catalysts, for instance nickel-alumina steam reforming catalysts and copper-zinc catalysts for low temperature water gas shift reaction and methanol synthesis [4, 5]. In principle, active metal ions and support ions are co-precipitated either as hydroxides or hydroxy salts. A homogeneous active precursor distribution can be obtained by the use of this technique, but catalyst accumulation is hard to control and suffers reproducibility problems [1].

In the second category, an excellent review of sol-gel process has recently been provided by Ko [6]. Sol-gel processes are the methods to prepare dispersed materials through the growth of metal oxo polymers in a solvent [7].

The basic principle of this process involves the formation of a sol that is a liquid suspension of solid particles ranging from 1 nm to 1 micron which is obtained by hydrolysis and partial condensation of a starting material (either an inorganic salt or a metal alkoxide), followed by formation of a gel which can be produced either by further sol condensation into a three dimensional network or by destabilising a solution of preformed sols [6].

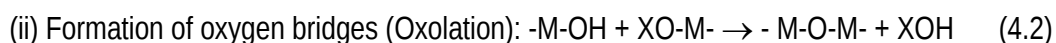
Sol-gel chemistry of metal alkoxides can be simplified [6, 8, 9] in terms of the following reaction equations :



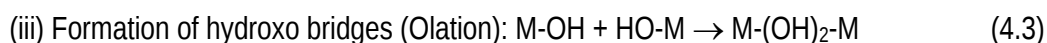
The mechanism involves (a) nucleophilic attack of the metal M by the oxygen atom of a water molecule, (b) transfer of a proton from the water to an OR group of the metal and (c) release of the resulting ROH molecule [9].

As soon as reactive hydroxy groups are obtained, the formation of branched oligomers and polymers with a metal oxo based skeleton and reactive residual hydroxo and alkoxy groups occurs through a polycondensation process [9].

Two mechanisms have to be considered, depending on the experimental conditions [6, 8, 9]



In this case X means either a H or R (an alkyl group). Oxolation is also a three step nucleophilic substitution reaction which occurs through the elimination of H₂O or ROH. Generally, under a stoichiometric hydrolysis ratio ($h = H_2O/M < 2$) the alcohol producing condensation is favoured, whereas the water forming condensation is favoured for larger hydrolysis ratios ($h \gg 2$) [7, 9]



This is a nucleophilic addition reaction that can proceed when the coordination of the metallic centre is not fully satisfied ($N-Z > 0$, where Z is the valence or the oxidation state of the metal). The hydroxo nucleophilic group enters the unsaturated coordination sphere of the metal. Olation does not need the proton transfer (i.b) and the removal of a leaving group (i.c). Thus, the kinetics of olation are usually faster than oxolation [9, 10].

The hydrolysis, oxolation and olation are responsible in the transformation of a metal alkoxide precursor to a metal oxo macromolecular network. The recombination of these metal oxo polymers lead to produce well dispersed structures which invade the whole volume [9]. When these oxo polymers reach macroscopic sizes, the reaction bath becomes a gel, inside which, the solvent, reaction by-products and free polymer are trapped. If the polymerised structures do not reach macroscopic sizes, sols are produced. Precipitates are formed if the reactions produce dense rather than well dispersed structures [7, 9].

The advantages of using sol-gel process includes the ability of maintaining high purity, changing physical characteristics such as pore size distribution and pore volume, varying compositional homogeneity at a molecular level, preparing samples at low temperatures, incorporating multi components in a single step, and producing different physical forms of samples. Table 4.1 shows a summary of the key steps in a sol-gel process which includes the aim of each step along with experimental parameters that can be manipulated [6].

Table 4.1 Important parameter in the various steps of a sol-gel process [6]

Step	Purpose	Important parameters
Solution chemistry	to form a gel	Type of precursor; Type of solvent; pH(acid/base content); Water content; Precursor concentration; Temperature
Aging	To allow a gel to undergo changes in properties	Time; Temperature; Composition of the pore liquid (e.g. pH); Aging environment (e.g. humidity)
Drying	To remove solvent from a gel	Drying method (e.g. evaporative vs. supercritical vs. freeze drying); Temperature and heating rate; Pressure and pressurization rate; Time
Calcination/sintering	To change the physical/chemical properties of the solid, often resulting in crystallisation and densification	Temperature and heating rate; Time; Gaseous environment (e.g. inert vs. reactive gases)

With respect to the drying methods, supercritical produces aerogels which are usually obtained as very fine powders or fragile monoliths. These properties are not desirable in industrial catalysts [11] despite the fact that the products exhibit a very high surface area in contrast to xerogels which are produced by evaporative drying.

4.2.2 The route to cerium and cerium doped oxides

Ceria is a well established component in three way catalysts due to its ability to store and release oxygen. This property is commonly known as oxygen storage capacity (OSC) [12]. A major drawback of ceria is poor thermal stability at elevated temperature [13]. Attempts have been made for years to dope ceria, either with isovalent cations such as zirconium or aliovalent cations namely yttrium, gadolinium, and samarium.

4.2.2.1 Doping ceria with isovalent cation (zirconium)

(Ce,Zr)O₂ mixed oxides have been the subject of extensive research in the last few years, resulting in a commercially produced car exhaust catalyst [14-17].

Cuif et al. [18] observed the enhancement of OSC performance due to thermally stable of (Ce,Zr)O₂ solid solution when in used with platinum. The term solid solution means that there is an intimate association within a unique phase (a solid state) of components in varied proportion. It was reported that a pure cubic solid solution could be obtained even up to cerium substitution of 50 mole %. Platinum was deposited on to the mixed oxides support by ion-exchange and the support was prepared by a proprietary co-precipitation

route. The surface area of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ was found to lie between 40 - 50 m^2g^{-1} after aging at 900°C for 6 hours.

Zirconia rich compositions of more than 50 wt% of (Ce,Zr) O_2 mixed oxides, coupled with small amounts of (proprietary) stabilizers, exhibited enhancement of OSC of ceria as observed by Mussmann et al. [19]. The surface area of the fresh sample was 44 m^2g^{-1} and it lost only 16 % of its initial surface area (to 37 m^2g^{-1}) after aging at 900°C for 10 h. A combined impregnation and co-precipitation route of Pd/ (Ce,Zr) O_2 mixed oxides catalysts was chosen.

Thermal stabilisation of Rh/Ce O_2 by the insertion of Zr O_2 was also claimed by Yamada et al. [20]. Depending on the ceria/zirconia ratio, the surface area was between 10 to 30 m^2g^{-1} after aging in air at 900°C for 5 h, but no initial values were reported. No preparation techniques for mixed oxides was reported, despite the fact that monolithic substrates with a washcoat containing proprietary stabilizers were used.

Nunan [15] observed similar enhancements in the redox activity of (Ce,Zr) O_2 mixed oxides supported on to $\gamma\text{-Al}_2\text{O}_3$ in comparison to non-supported mixed oxides. Neither solid solution procedures nor surface areas of prepared samples were reported.

Vlaic et al. [21] observed the improvement of Rh/(Ce,Zr) O_2 mixed oxides redox properties over Rh/Ce O_2 which has been attributed to a low temperature reduction in the bulk. The insertion of Zr^{4+} into the Ce O_2 lattice modified the O_2 sub-lattice which, in turn, generated mobile oxygen in Rh /Ce $_{0.5}\text{Zr}_{0.5}\text{O}_2$. The mixed oxides support was prepared by firing a mixture of appropriate composition of oxides at 1600 °C followed by quenching the

precursor to room temperature before Rh was loaded on to support by incipient wetness. No surface areas were reported.

Ceria rich (70 mol %) (Ce,Zr)O₂ mixed oxides were significantly changed in structure at 900°C, resulting in decreasing surface area (initially from about 50s m² g⁻¹ to about 20s m² g⁻¹) [22]. The samples were prepared by precipitation of cerium nitrate salt and zirconyl nitrate salt by the use of ammonium solutions up to pH 10. The maximum amount of surface oxygen-deficient sites for catalysing N₂O decomposition was observed at 900°C. Moreover, the synergistic effect of added rhodium was suggested to enhance mixed oxides reduction.

The effect of preparation methods on the properties of zirconia-ceria was studied by Rossignol et al. [23, 24]. Sol-gel routes produced homogeneous compounds of fluorite-type structure, even up to about 0.9 ceria mole-fraction. This is in contrast to the observed tetragonal zirconia, in which mixed oxides was prepared by coprecipitation. The surface area of the sol-gel samples were between 35 m²g⁻¹ to 45 m²g⁻¹ at a calcination temperature of 900°C regardless of the zirconium precursor, and excellent OSC properties as well as high thermal stability were claimed. However, no surface areas of samples prepared by co-precipitation route were reported. The effect of a lanthanum impurity of 1 % improved thermal stability of mixed oxides, despite the fact that the OSC decreased.

A higher surface reducibility and associated vacancy defects at lower temperatures compared to ceria was reported by Martinez-Arias et al. by employing EPR characterisation methods [25]. An equimolar ratio of ceria-zirconia sample was prepared by co-precipitation using microemulsions of zirconyl nitrate, cerous nitrate hexahydrate

and tetramethylammonium hydroxide pentahydrate. Regrettably, no surface area values were reported.

Using a commercial ceria-zirconia mixed oxide, Vidal et al. [26] observed OSC at low temperatures independent of zirconia composition. The stability of the properties were reported even after a redox cycle. For pure ceria, no reducibility was evident below 500°C. The surface area of the fresh sample was in the vicinity of 100 m²g⁻¹.

Vidmar et al. [27] observed the improvement of OSC at low temperatures in that the reduction temperature decreased with the bulk of solid solution of Ce_{0.6}Zr_{0.4}O₂. Sol-gel routes were employed by the use of nitrate salts of cerium and zirconium complexed by citric acid as previously suggested by Courty et al. [28]. The precursor was calcined at 500°C for 5 hours and the surface area was 89 m²/g. No surface areas at elevated temperatures were reported. Using different methods, Fornasiero et al. [29-31] reported that the surface area of Ce_{0.5}Zr_{0.5}O₂ prepared by the citric acid route was in the vicinity of 40 m²g⁻¹, in contrast to the alkoxide route prescribed by Mariani and Soraru [32] which gave 65 m²g⁻¹. The latter technique suffered solubility limitation when one tried to incorporate the third component as will be demonstrated in the following section.

4.2.2.2 Doping ceria with alio-valent or mixture of iso and alio valent cations

Rare-earth components were used as dopants for obtaining ceria based solid solutions [33-40] and the improvement of ceria performance was discussed in the context of increasing ionic conductivity. The ability of the oxygen ions to move through the metal-ion

lattice is a measure of the ionic conductivity of metal oxides. The higher the ionic conductivity, the easier and quicker oxygen ions move inside the lattice and the more oxygen vacancies are created with associated higher oxygen mobility. Sm, Gd, and Y dopants give the highest values in ionic conductivity and the solid solutions were prepared by ball milling ceria powder with appropriate amount of dopants; No surface area values were reported [34-41]. Even though bismuth oxide is considered to be the most electrically conductive material, this particular oxide is structurally unstable.

The insertion of one of the trivalent cations (namely Y, La, and Ga) into $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ improves its OSC at low temperatures by decreasing the temperature of the reduction in the bulk of mixed oxides relative to the undoped mixed oxides [27]. The surface areas of doped samples are quite high, (between 79 to 111 m^2g^{-1}) depending on the type and dopant content. Citric acid route sol-gel is used as previously described in the preparation for $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$.

More recently, Shigapov et al.[42] reported that PrO_yCeO_2 exhibited a better OSC compared to ceria-zirconia at temperature $\leq 350^\circ\text{C}$. Mixed oxides were prepared by an organic-templating method. In this case a Whatman 50 filter paper (considered as a high purity microcrystalline cellulose material) was completely wet with the required amounts of starting materials followed by drying and combustion of the cellulose at 650°C . The fresh equimolar composition of praseodymia-ceria oxides gave a surface area of 36 m^2g^{-1} .

In conclusion, the performance of ceria can be improved either by insertion of isovalent cations and in particular zirconium ion, or aliovalent cations, or even a combination of iso

and alio cations. The mixed oxide samples can be prepared by various ways, namely precipitation, mixing and high energy milling, as well as by the sol-gel route. More emphasis will be focused on the latter method as the most promising route in the context of catalysis.

4.3 Catalyst characterisation

4.3.1 Surface measurement

4.3.1.1 Total surface area

The total surface area measurement was carried out by using multi point methods. Both an ASAP 2000 and a Tristar surface area analysers were employed. The sample of ca. 0.3 grams was first loaded in a round bottom sample tube, dried and degassed at 120 °C under helium for about four hours and then cooled to liquid nitrogen temperature (-196 °C) by immersing the sample tube into liquid nitrogen. The analysers automatically measured, recorded, and calculated nitrogen adsorption at various pressures. In principle, the amount of adsorbate (nitrogen) required to form a mono layer of molecules on the catalyst surface is determined by the following equation [43]:

$$\frac{P}{V_a(P_o - P)} = \frac{1}{V_m C} + \frac{(C-1) P}{V_m C P_o} \quad (4.4)$$

Where, V_a is the volume of gas adsorbed at pressure P

P_o is the gas saturation pressure;

V_m is the volume necessary to cover the entire adsorbing surface by a monomolecular layer;

and C is a constant involved with energy of adsorption.

A plot of $P/(V_a(P_0 - P))$ versus relative pressure of P/P_0 in the range of 0.05 to 0.3 yields a straight line with the intercept of $1/(V_m C)$ and a slope of $(C - 1)/(V_m C)$ respectively. The volume of gas required to form an adsorbed monolayer of V_m and the surface area per gram of catalyst sample of S can be determined by

$$S = \frac{V_m A_m N_a}{W V_0} \quad (4.5)$$

Where, S is the specific surface area of the sample in $\text{m}^2 \text{g}^{-1}$;

N_a is the Avogadro's number ($6.023 \times 10^{23} \text{ molecules mol}^{-1}$);

A_m is the area of an adsorbed molecule ($16.210 \times 10^{-20} \text{ m}^2 \text{mol}^{-1}$);[44]

V_0 is $22414 \text{ mL mol}^{-1}$; and

W is the catalyst weight after analysis (g).

4.3.1.2 Metallic surface area

The active metal surface area, and metal dispersion of the catalysts were determined by hydrogen-pulse chemisorption measurements using a Micromeritics Autochem 2910 analyser. An exact amount of sample (ca. 0.3 grams) was weighed and placed into the U-tube sample bulb between two wads of quartz wool. The manifolds were degassed under helium at room temperature followed by injection of hydrogen to reduce the sample at 600

°C (5 °C min⁻¹) for four hours. The sample was then degassed at 600 °C, and cooled to 50°C. The hydrogen gas was then introduced in the manifold volume and the pressure was measured. The manifold contents were then allowed to expand into the sample bulb volume until equilibrium was achieved.

The amount of gas adsorbed onto the surface of the sample was determined by employing the ideal gas law and converting to volume adsorbed at 0 °C and 760 mmHg. Repeated pulses were carried out in the pressure range of 0.5 – 400 mmHg until the active sites have completely reacted (the discretely injected gas volumes emerged from the sample tube unchanged). The gas irreversibly adsorbed related to the active surface area was obtained by subtracting the total amount of hydrogen injected and the amount of hydrogen that did not react with the active sites of the sample [44]. In principle the metallic surface area of a sample was calculated according to the following equation [43]:

$$S_m = \frac{6.023 \times 10^{23} V F_c A}{22414} \quad (4.6)$$

Where, S_m is the metallic surface area (m² g⁻¹);

V is the amount of hydrogen chemisorbed on the sample (cm³ g⁻¹);

F_c is the calculated stoichiometry factor depending on adsorbate and metals on the catalyst;

A is the effective area of one active metal atom (m² atom⁻¹).

The flow rates of all gases used were individually set at 15 mL min⁻¹. The whole operations were controlled automatically by a personal computer. The sequences of experiments were programmed in the provided program editor. Once a sample was loaded

in the sample tube and all required cylinder gases were ready, the next step involved running the program.

4.3.2 Thermal methods of catalyst characterisation

Thermal techniques such as temperature programmed reduction (TPR) and temperature programmed oxidation (TPO) are known as some of the most useful methods for the determination of chemical properties of catalysts [43, 45]. They show the quantity of the reductant/oxidant required for the reduction/oxidation of catalysts (and thus the degree of oxidation of the metal in catalysts), the temperature range at which the catalysts should be reduced (or oxidised) as well as giving information about species formed during the treatment of the catalysts according to the extent of reducibilities of different species [45, 46] .

In this study, TPR and TPO methods were employed to investigate the temperature range for the reduction/oxidation of the samples. All experiments were performed sequentially (TPR first, followed by TPO) using the same catalyst sample loaded in the U-tube sample bulb in a Micromeritics Autochem 2910 analyser. Approximately 0.3 grams of catalyst was loaded in the sample bulb and inserted into sample tube manifold. The catalyst was degassed under nitrogen at 350 °C and held for one hour to degas the moisture content, then cooled to ambient temperature. The temperature was then programmed from ambient temperature to 600 °C at a ramp rate of 2 °C min⁻¹ under 5% hydrogen in nitrogen flow rate of 15 mL min⁻¹. The change of thermal conductivity signals corresponding to the hydrogen uptake were recorded and collected automatically by an on-line computer system as previously described for the chemisorption experiments.

The sample was then cooled to ambient temperature under helium. A mixture of 1% oxygen in helium was passed over the sample. While oxygen was flowing, the sample temperature was increased to 600 °C at a ramp rate of 2°C min⁻¹. The change of thermal conductivity signals corresponding to the oxygen uptake were recorded and collected automatically as previously described.

4.4 Experimental

4.4.1 Preliminary experiment

4.4.1.1 Preparation of alumina support by sol-gel

Alumina has been known for a catalyst support [47]. The most common methods for preparing alumina gels was developed by Yoldas [48, 49] involving hydrolysis of aluminum isopropoxide (AIP) or aluminium sec. butoxide (ASB) in excess water and catalysed by inorganic acid. However, in the context of metal supported catalysts, the gelation of aluminium hydroxide occurred very rapidly, resulting in a non-homogeneous co-gel. As a result, urea was added to control the rate of hydrolysis of aluminium hydroxide. The urea decomposed in the solvent to give ammonium hydroxide ions, by which the pH of the sol gradually increased whilst the ζ - potential of the sol gradually decreased, resulting in a gradual gelation of the boehmite ($\text{AlO}(\text{OH})$) sol [50]. This finding was the basis for the following preparation recipe

- (i) Aluminum sec. butoxide (26 mL) was hydrolysed under reflux with hot milli-Q water (80 mL, 90°C) in a round bottom flask mounted in a heating mantle. The resulting cloudy sol was stirred continuously. The mixture bubbled after 15 min of operation. The heating mantle was switched off to cool the sol well below 90 °C and the stirrer was switched off

- (ii) After ca. 3 min, the heating mantle and the stirrer were switched on again and a small amount of nitric acid (1N, 10 mL) was added to the sol after 30 min of stirring. A clear sol gradually occurred
- (iii) About 3 g urea was added drop wise to the sol after 30 min of stirring. Gel formation occurred within 30 min. The heater and stirrer were switched off
- (iv) The resulting gel was soaked 2 nights in ethanol (ca. 500 mL)
- (v) The gel was filtered and dried overnight (120°C), prior to calcining in air (600 °C, 1°C min⁻¹, 4 h)

4.4.1.2 Preparation of a nickel based catalyst by sol-gel

This first trial (Section 4.4.1.1) indicated that handling ASB in an excess water was not easy. Moreover, ASB is very moisture sensitive. As a result, the concept of partial hydrolysis of ASB [51, 52] and handling this material under nitrogen in either an atmosbox or an atmosbag was applied for preparing a NiO/CeO₂/Al₂O₃ catalyst.

- (i) Exact amounts of 2.042 g cerium nitrate hexahydrate was dissolved in 50 mL ethanol, poured into a five-neck round bottom flask mounted in a heating mantle and stirred under reflux at ambient temperature for 10 min, resulting in a yellowish transparent sol
- (ii) In a separate beaker and under nitrogen, 25 mL aluminium secondary butoxide (ASB) was dissolved in 200 mL hot ethanol (80 °C) and stirred about 30 min. This was mixed with (i), resulting in a clear sol (pH 6.5)

- (iii) Milli-Q water (1 mL) was dissolved in 100 mL hot ethanol (80°C) and mixed with (ii), resulting in a cloudy sol (pH 6.1). Addition of a further 50 mL cold ethanol did not make the sol clearer
- (iv) Exact amounts of 19.249 g nickel acetate was dissolved in 150 mL hot ethanol (80°C). This was mixed with (iii), resulting in a green transparent sol (pH 5.5). The sol was stirred for 3 hours and the temperature was kept at 80 °C. The sol was then gradually cooled to ambient temperature and the stirrer was turned off in order to investigate the possibility of precipitation of any precursor
- (v) Additional milli-Q water (2.6 mL) was dissolved in 100 mL cold ethanol and poured into (iv). The sol was continuously stirred again for 15 min (pH 5.9)
- (vi) The stirrer and reflux system were turned off, and the sol was aged for 3 days at ca. 75 °C. The sol gradually transformed into a well dispersed structure and the pH of remaining sol was stable within 5 – 5.2
- (vii) On the fourth day, the resulting gel was dried in an oven (120 °C, overnight) prior to calcining in air, in a muffle furnace (600°C, 4 h).

The resulting catalyst had a nominal composition of 35% NiO/ 5% CeO₂ / 60% Al₂O₃ and subject to test for fuels conversion [53].

4.4.1.3 Preparation of ceria-based mixed oxide supports by sol-gel

Initial experiments to prepare ceria-zirconia solid solutions were carried out by employing a modified Meriani-Soraru method [32]. Instead of Zr-tetra-n-butoxide, Zr-isopropoxide was

used as a starting material along with cerium(III) acetylacetonate. Moreover, azeotropic distillation techniques to purify Ce-ethanol mixtures was also introduced.

To obtain 5 g of final mixed oxides, 8.565 g of cerium salt was partly dissolved firstly in 100 ml of ethanol, followed by subsequent dissolution in 50 ml of the same solvent until all of the cerium salt was dissolved in 550 ml ethanol. This was needed 30 min of operation under stirring and heating (50- 60°C). A 5-neck round bottom flask reactor mounted in a heating mantle and equipped with an of azeotropic distillation apparatus [54] was used. The distillation was then carried out and the first distillate came-off at 75°C±0.5°C. After 90 min of distilling the mixture, the temperature rose gradually and 7.2 ml of Zr-isopropoxide formerly dissolved in 100 ml cold ethanol was added drop-wise to the reactor. The reactor temperature dropped suddenly to 60°C but it rose again after a few minutes.

Exactly 0.582 g of water was added by a syringe into the mixture 2 hours after the Zr-propoxide addition step. Ten minutes later, the stirrer was switched-off and the distillation apparatus was turned -off, followed by aging of the mixture at 60°C for 24 hours. A small amount of brown jelly-like material was obtained, which was dried overnight at 120°C. A dish of dark-brown cake was then calcined in air at 600°C for 4 hours at a heating rate of 1°C min⁻¹. The resulting yellowish cake was then ground for surface area measurement. The area of the mixed oxides was found to be 30.6 m² g⁻¹, which was about half of similar oxides prepared by Fornasiero et al.[29, 31]. A direct comparison was not appropriate since they calcined the precursor at 500°C.

A second attempt involved the preparation of ceria-yttria oxides prior to preparing ceria-zirconia-yttria oxides by the same route. However, the mixture suffered solubility limitations even though the amount of yttrium doping was as low as 5 wt% (final Yttria).

An alternative route should, therefore, be sought and the success of the citric acid route of Courty et al. [28] and more recently Vidmar et al. [27] was a good choice to start with.

An attempt was then made to prepare ceria-zirconia mixed oxides by following the route as exactly prescribed by Vidmar et al. [27]. This was unsuccessful due to solubility limitation. The problem occurred just after the addition of Zr precursor. To a certain extent, an understanding of the genesis of zirconia and the complex hydroxides of zirconium is mandatory.

Hydrous zirconia, which is designated as $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$, implies that the water is loosely bound in non stoichiometric proportions [55]. It is known that ions and molecules which complex zirconium tend to inhibit or prevent the formation of hydrous zirconia when the pH of a zirconyl salt solution is raised. When the stoichiometric amounts of citrate, tartrate, lactate, or certain complexing ions are present, the precipitation of hydrous zirconia is prevented until the pH attains a strongly alkaline value of ca. 10-11 [56].

Studies made by Hagiwara [57] on heating sulfate solutions of various transition elements to 90°C provided some idea to avoid zirconium precipitation. It was reported that zirconium was precipitated at pH 2.8, while yttrium and cerium were at pHs 6.3 and 2.4 respectively. This means that, if the pH of Ce, Zr, and Y can be adjusted to a level more acidic than that of their respective precipitation values, the solubility limitation may be overcome. Unfortunately any pH measurement in methanol medium is impossible, and a series of experiments of pH adjustment by nitric acid addition were carried out using milli-Q water. It was found that a pH of ca. 1 was sufficient to avoid unwanted precipitation of either Ce, Y, or Zr. The amount of nitric acid required to alter the pH of the solution relative to the

starting materials was then adopted to the system using methanol as solvent, and the success of preliminary trials were documented as the mixed-oxides recipe in the following section.

4.4.2 Establishment of catalyst recipes

4.4.2.1 Mixed Oxides (MO) support preparation

MO were prepared firstly by the addition of zirconyl nitrate hexahydrate dissolved in methanol (MeOH) (0.1 M, 300 ml) into citric acid dissolved in methanol (0.5 M, 140 ml) followed by the addition of cerium (III) nitrate hexahydrate (17.08 g in MeOH, giving a total solution of 100 ml) to the first mixed salts solution. Prior to mixing, a diluted nitric acid solution (35 wt%) was added to zirconyl salts solution (15 ml), to the citric acid solution (15 ml), and to the cerium salt solution (20 ml) respectively. The resulting sol was then stirred in room temperatures overnight followed by evaporation of MeOH in a Rotavapour at 50 °C for 0.5 to 5 hours under vacuum (depending on the vacuum conditions). The yellowish transparent syrup was then dried in a vacuumed oven at 70 °C overnight. The dried foamy gel was then flash-decomposed at 500 °C for 30 min followed by a step wise calcination in air (500 °C -5 hours; 600 °C -2 hours; 750 °C -2 hours) at a heating rate of 5 °C min⁻¹.

4.4.2.2 Metal oxides catalysts

Pt, Rh, and Ni catalysts were prepared by wet impregnation of MO support with a solution of the respective salts. Each precursor was stirred manually for 3 hours at 50-60 °C, then dried in an air oven at 120 °C overnight. The dried cake was calcined in air at 750 °C for 4 hours at a heating rate of 5 °C min⁻¹. The final catalysts gave a nominal composition of 1 wt% of Pt/Rh, 2 wt% of Pt and 5 wt% of Ni as metal.

For safety reason, it is not advisable to prepare heavy metals/mixed oxides catalysts in a single step of sol-gel method under nitric acid and alcohols (nital) environment since fulminates capable of detonating the mixture may be formed [58].

The Rh/CeO₂/δ-Al₂O₃ catalyst was prepared by a sequential impregnation method. γ-Al₂O₃ was crushed using a mortar and pestle to a particle size range of 300-500 microns. It was then heated in a muffle furnace at 1000°C in air for 4 hours. This has the desired effect of converting the γ-Al₂O₃ to δ-Al₂O₃. This phase change was confirmed by XRD and surface area measurements.

Exact amounts of 2.25 g cerium acetate hydrate was dissolved in 100 mL milli-Q water and added drop wise to 10 g δ-Al₂O₃. The mixture was heated to ca. 70 °C and stirred continuously overnight. The dry precursor was then calcined in air at 600 °C (heating rate: 1°C min⁻¹) for 4 hours. 3.4 mL of rhodium nitrate solution was diluted to 100 mL with milli-Q water and added drop wise to 10.64 g CeO₂-δ-Al₂O₃ support. A similar drying and calcination procedure as mentioned above was followed to prepare the Rh/ CeO₂-δ-Al₂O₃. The resulting catalyst contained 1% Rh and 10% CeO₂ by weight.

The NiO/ CeO₂- δ -Al₂O₃ catalyst was prepared by the same methods employed to make the Rh/CeO₂- δ -Al₂O₃ sample. Exact amounts of 10.509 g nickel acetate hydrate was dissolved to 100 mL milli-Q water. The mixture was then added drop wise to 5.737 g CeO₂- δ -Al₂O₃. A similar drying and calcination procedure was followed to prepare the NiO/ CeO₂- δ -Al₂O₃ sample. The resulting catalyst contained 35% NiO and 5% CeO₂ by weight.

All catalysts prepared by a sequential impregnation method were sieved to 300 – 500 microns before use.

4.4.2.3 Pt/Ni-com catalyst

A Pt/Ni-com catalyst was prepared by wet impregnation of a commercial NiO/MgO/Al₂O₃ steam reforming catalyst with a solution of tetraamine platinum chloride. The precursor was stirred (60 °C : 3 h), dried (120 °C : 12 h) and calcined (500 °C : 4 h) before use. The catalyst was crushed and sieve to 300 – 425 microns.

4.5 Results and discussions

4.5.1 Ceria-Zirconia mixed oxides

4.5.1.1 Effect of nitric acid addition technique on the BET surface area

A Ce_xZr_(1-x) O₂ sample where $0.5 \leq x \leq 0.6$ by mole fraction was prepared according to the method described in Section 4.3.2.1 except that 70 wt% of HNO₃ was used without

dilution. The nitric acid/starting materials molar ratio was kept constant as prescribed by the method. After dissolving the cerium salt and the zirconium salt in methanol individually, a required amount of HNO_3 was dropped into the dissolved cerium salt as well as into the dissolved zirconium salt. The two solutions were then mixed. A very clear sol was obtained and the final product after drying and calcination gave a surface area of $44.4 \text{ m}^2 \text{ g}^{-1}$ which was comparable to the results reported by Fornasiero et al. of ca. $40 \text{ m}^2 \text{ g}^{-1}$ [29] for an equimolar composition of ceria-zirconia mixed oxides.

For the sake of safety, it was intended to dilute HNO_3 from 70 wt% to 35 wt% but keeping the same molar ratio of acid/starting materials.

In order to study the influence of different injection techniques of nitric acid, the procedure was repeated using diluted HNO_3 . In this case, each of starting materials was mixed with methanol and the acid at the same time. For zirconium salt solutions, a small amount of white precipitate occurred which was believed to be hydrous zirconia. On mixing all dissolved starting materials in a one beaker, followed by stirring overnight, the white precipitate could not be dissolved. The surface area of final product decreased dramatically to $25.3 \text{ m}^2 \text{ g}^{-1}$.

The procedure was repeated once again by employing diluted HNO_3 of 35 wt%, however, the acid injection technique was the same as first experiment. No acid addition was done unless complete dissolution of any starting material was evident. A very clear sol was obtained and the surface area of the final mixed oxides was found to be $43 \text{ m}^2 \text{ g}^{-1}$ - within the expected experimental error of the first experiment.

From these experiments, it can be inferred that the method of acid injection influences the final surface area due to the partial formation of hydrous zirconia. The rate of partial hydrolysis of zirconium salt to produce hydrous zirconia is faster than the rate of dissolution of zirconium salt in methanol, and a good dispersion of zirconium ion in the host lattice of cerium ion is not achieved. There is no problem of diluting HNO_3 for safety reasons as long as the molar ratio of acid to starting materials is kept constant. This finding was then used as the basis for the preparation of other ceria based mixed oxides.

4.5.1.2 Effect of calcination temperature towards BET surface area

The effect of thermal ageing of ceria-zirconia mixed oxides was studied by measuring surface areas from the same initial batch at 500°C, 600°C, and 750°C respectively. Comparison was made to pure ceria prepared by same method and Table 4.2 summarises the results.

Table 4.2 Effect of calcination temperature towards BET of ceria and ceria-zirconia

Calcination temperature, °C	BET of ceria, $\text{m}^2 \text{g}^{-1}$	Normalised BET of ceria	BET of ceria-zirconia, $\text{m}^2 \text{g}^{-1}$	Normalised BET of ceria-zirconia
500	57.5	1	43	1
600	55.4	0.96	35.4	0.82
750	38.6	0.67	31.2	0.73

Error of measurement: $\pm 1\%$

It is seen that the pure ceria surface area obtained is relatively high compared to ca. $20 \text{ m}^2 \text{ g}^{-1}$ as reported by Kay et al. [59], even though the purity of ceria salt used was only 99 % and a higher calcination temperature (ca. 100°C) was applied. The difference in surface area may result from the different solvent used, despite the fact that the basic preparation method was the same. While this study employed methanol as a solvent, the former used water - which may give a higher hydrolysis rate of reaction relative to methanol. This, in turn, may cause a partially premature precipitation of the starting material. Additional experiments using water as a solvent were carried out for the preparation of ceria-zirconia mixed oxides and only a thin layer of white precipitate upon aging of the mixture was occurred.

From the normalised surface areas of pure ceria, it is clear that thermal stability of ceria is relatively stable up to 600°C , however, it loses 33 % of its initial surface area upon calcining at 750°C . Surprisingly, ceria-zirconia loses ca. 18% of its surface area at 600°C , despite the fact that at a higher temperature it seems more thermally stable than pure ceria. Further calcination of mixed oxides at 900°C gives a surface area of ca. $16 \text{ m}^2 \text{ g}^{-1}$ or a loss of surface area of 63 %. A commercial ceria-zirconia mixed oxides [60] exhibited a very high initial surface area of $143 \text{ m}^2 \text{ g}^{-1}$ but the calcination temperature was unknown. When sintered at 900°C for 6 hours, 73 % of the initial surface area was lost.

4.5.1.3 Effect of cerium nitrate impurities towards BET surface area

All cerium nitrate salts used in the previous experiments contained lanthanum between 1 - 2 wt.%. An attempt was made to study the effect lanthanum by the use of pure cerium

nitrate salt (99.99 %) as a starting material for the preparation of ceria-zirconia mixed oxides by the same recipe as well as the same cations composition. The zirconyl nitrate salt was kept the same as previously described. Surface areas were measured results are summarises in Table 4.3.

Table 4.3 Effect of lanthanum towards surface area of ceria-zirconia

Calcination temperature, °C	BET of ceria-zirconia, m ² g ⁻¹	Normalised BET of ceria-zirconia	BET of ceria-zirconia, m ² g ⁻¹ (p)	Normalised BET of ceria-zirconia (p)
500	43	1	28.4	1
600	35.4	0.82	26.4	0.93
750	31.2	0.73	18.8	0.66

(p) : pure cerium nitrate salt; error of measurement: ± 1%

From Table 4.3, it is clearly seen that pure cerium nitrate salt exhibited smaller surface area values at all calcination temperatures despite the fact that, at 600°C, the sample gave a better thermal stability.

It is therefore reasonable to suggest that lanthanum stabilises the prepared mixed oxides, probably due to a better dispersion of zirconium ion in the host cerium lattice. This finding is in agreement to previous results [23, 24].

4.5.2 Ceria-Yttria mixed oxides

A Ce_{0.95}Y_{0.05}O₂ was prepared by same technique and a series of sintering test was undertaken. The following table represents the main findings:

Table 4.4 Effect of calcination temperature towards BET of ceria-yttria

Calcination temperature, °C	BET of ceria-yttria, m ² g ⁻¹	Normalised BET of ceria-yttria, m ² g ⁻¹
500	42.0	1
600	38.2	0.91
750	13.6	0.32

Error of measurement: $\pm 1\%$

It is apparently seen that the initial surface area of ceria-yttria is almost the same as ceria-zirconia. The decreasing surface area compared to pure ceria is probably due to pore blockage of the ceria host lattice by the insertion of a dopant. It is not surprising that ceria-yttria gives a better thermal stability at 600°C and a lower stability at 750°C, since this particular composition is richer in ceria.

4.5.3 Ceria-Zirconia-Yttria mixed oxides

The last experiment of the preparation of ceria based mixed oxides involved a combined iso and alio valent dopants of $\text{Ce}_{0.6}\text{Zr}_{0.35}\text{Y}_{0.05}\text{O}_{1.975}$ and the samples were also subjected to a series of thermal ageing.

Table 4.5 Effect of calcination temperature towards surface area of ceria-zirconia-yttria

Calcination temperature, °C	BET of ceria-zirconia-yttria, m ² g ⁻¹	Normalised BET of ceria-zirconia-yttria, m ² g ⁻¹
500	33.0	1
600	33.7	1
750	17.2	0.52

Error of measurement: $\pm 1\%$

This table shows that the insertion of a trivalent dopant provides excellent enhancement of ceria thermal stability up to 600°C, above which a substantial loss of surface area of ca. 50 % is evident. Perhaps this can be attributed to the structural instability of the yttrium dopant at an elevated temperature.

4.5.4 Catalysts properties

Apart from the results reported in Section 4.5.1 - 4.5.3, Table 4.6 and 4.7 show catalyst specifications and their surface properties respectively.

Table 4.6 Catalyst specifications

Sample	Nominal composition/ wt%	Source	Remarks
1	γ -Al ₂ O ₃ (pure)	Laboratory	Sol-gel
2	1 Rh/ 99 γ -Al ₂ O ₃	Laboratory	Impregnation/sol-gel
3	CeO ₂ (pure)	Laboratory	Sol-gel
4	2 Pt/ 98 CeO ₂	Laboratory	Impregnation/sol-gel
5	60 CeO ₂ - 40 ZrO ₂	Laboratory	Sol-gel
6	1 Rh/ 60 CeO ₂ - 40 ZrO ₂	Laboratory	Impregnation/sol-gel
7	1 Pt/ 60 CeO ₂ - 40 ZrO ₂	Laboratory	Impregnation/sol-gel
8	1 Rh/ 10 CeO ₂ – 89 δ Al ₂ O ₃	Laboratory	Sequential impregnation
9	35 NiO/ MgO- Al ₂ O ₃	Commercial	-
10	35 NiO/ 5 CeO ₂ / 60 Al ₂ O ₃	Laboratory	Sol-gel
11	35 NiO/ 5 CeO ₂ / 60 Al ₂ O ₃	Laboratory	Sequential impregnation
12	2 Pt-98(NiO/ MgO- Al ₂ O ₃)	Lab./commercial	Impregnation/-
13	1 Pt/ 3Cr ₂ O ₃ / 96 SiO ₂	Laboratory	Sequential impregnation

Table 4.7 Catalyst surface properties

Sample	BET, m ² g ⁻¹	Pore dia., nm	Pore volume, mL g ⁻¹	Ni surface area, m ² g ⁻¹	Metal dispersion, %	Active particle dia., nm
1	387	-	-	-	-	-
2	-	-	-	-	-	-
3	27.7	7.1	0.057	-	-	-
4	26.4	7.6	0.056	-	-	-
5	30.6	2.4	0.018	-	-	-
6	12.8	6.2	0.022	-	-	-
7	16.4	3.4	0.014	-	-	-
8	142	18.5	0.66	-	-	-
9	11	21.2	0.06	0.51	0.3	33.7
10	210	3.7	0.20	-	-	-
11	94.5	14.2	0.34	-	-	-
12	9.9	17.5	0.12	-	-	-
13	118	11.2	0.33	-	-	-

Indeed, sample 10 and 11 indicate that sol-gel route gives a higher surface area and smaller particle diameter in comparison to impregnation methods. The results of hydrogen chemisorption measurements over sample 9 are consistent with the high (ca. 25% as Ni) metal loading on the support. As expected, the incorporation of a second metal (sample 4 and 12) to the parent support (sample 3) and parent catalyst (sample 9) slightly decreased their surface areas. The preparation methods of sample 13 was described elsewhere [53].

Sample 10 and 13 were used with fuels conversion experiments [53].

4.5.5 TPR and TPO results for the Ni-com catalyst

Figure 4.1 and 4.2 show TPR and TPO profiles for a commercial Ni-based catalyst. A bulk reduction temperature located at ca. 347 °C peak was comparable to ca. 300 °C as reported previously [61]. The shift in the peak is probably due to the different heating rate employed. Since the catalyst was supplied as a high temperature calcined solid, it is unlikely that the shoulder peaks at 270 °C and 395 °C are due to loss of promoters. However, they may be attributed to the reduction of low temperature metal aluminates. The absence of other peaks up to 600 °C showed that metal active sites for the steam reforming catalyst belonged to reducible metal oxides below this temperature. Above 400 °C, the sample was completely reduced. These results suggested that Ni-com catalyst was easily reduced. As a result, a reduction temperature of 600 °C was more than adequate. The peak oxidation temperature observed at ca. 400 °C is close to the bulk reduction temperature obtained during hydrogen TPR. In fact, oxygen uptake above 450 °C was negligible.

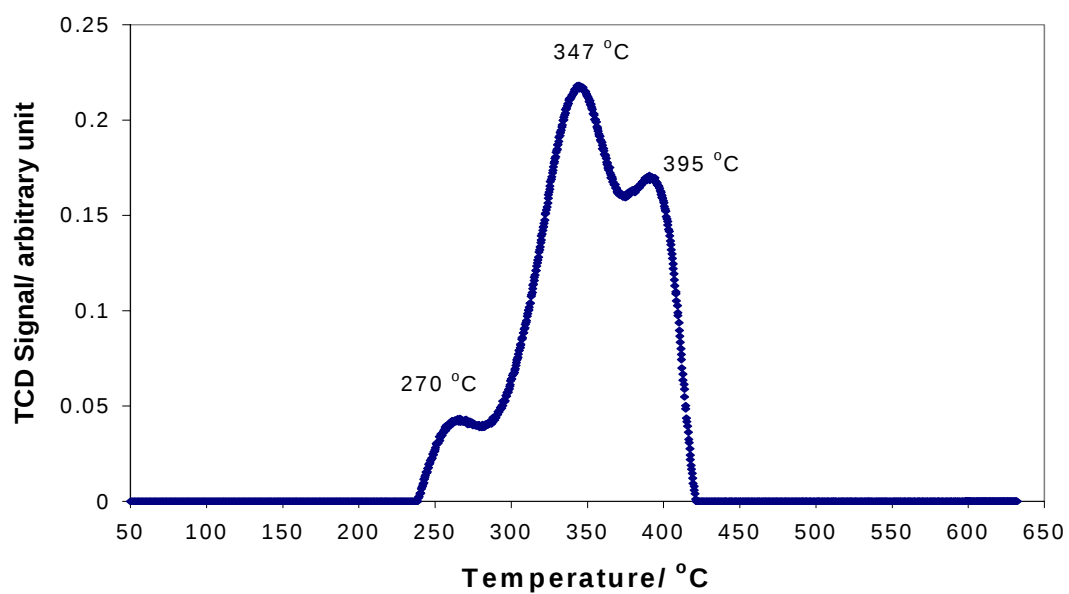


Figure 4.1 TPR profile for Ni-com catalyst (0.4 g, 10 mL min⁻¹; 5% H₂/N₂; heating rate 2 °C min⁻¹)

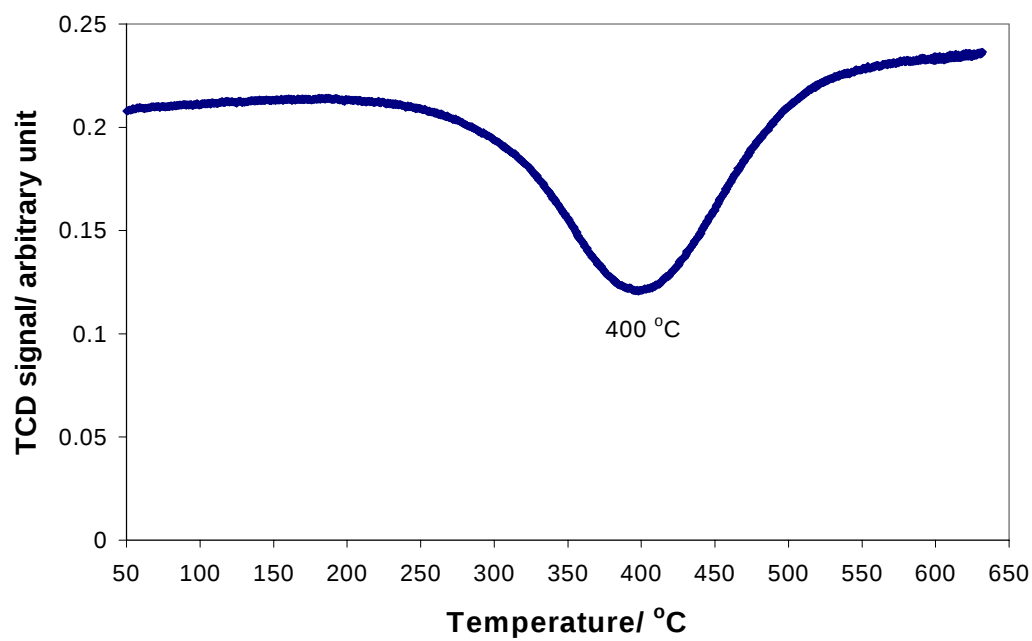


Figure 4.2 TPO profile for Ni-com catalyst (0.4 g, 10 mL min⁻¹ of 1% O₂/He, heating rate 2 °C min⁻¹)

4.6 Conclusions

Metal oxides catalysts were successfully synthesised over various supports. Even though sol-gel techniques had some advantages in comparison to conventional techniques (precipitation and impregnation methods), for safety reason a combination of sol-gel for the preparation of mixed oxides supports and wet impregnation for depositing transition metals on to the supports has found to be required.

4.7 References

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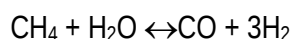
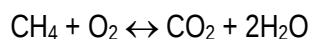
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Chapter 5 Partial oxidation of isooctane

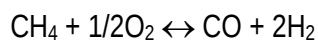
5.1 Introduction

The control of vehicle exhaust emissions using catalytic converters is well established [1]. However, increasingly stringent legislation has led to consideration of alternative means of reducing emissions, with fuel cell powered vehicles being considered in some depth [2]. The optimum unit for vehicle applications has been found to be the polymer electrolyte membrane fuel cell (PEMFC) but the cells have the disadvantage that they operate only on hydrogen as a fuel. Since the distribution of hydrogen is difficult and storage of hydrogen in a vehicle adds weight, consideration has been given to the conversion of more readily available fuels to hydrogen on board the vehicle.

Such conversion can be achieved by autothermal steam reforming, in which part of the fuel is oxidised to produce heat and part is steam reformed to produce hydrogen [3]



or by partial oxidation [4]



The partial oxidation of several fuels has been examined, ranging from methanol [5] to petrol [6]. The autothermal reforming of methane [7], methanol [8] and light hydrocarbons [9] has also been reported. The present study deals with the conversion of isooctane, used as a model for gasoline, to hydrogen



The investigation has been focused on the conversion of isooctane under oxygen deficient conditions pertinent to partial oxidation (reaction (5.2)) by the use of temperature programmed oxidation techniques (TPO). Rhodium based catalysts have been considered for the production of hydrogen by partial oxidation [10, 11] and steam reforming [10] but that the metal is very expensive and in short supply. As a result, some studies were carried out to see if there were a significant advantage in using rhodium (Chapter 5) over Pt/Ni-based catalysts (Chapter 6). In this case, rhodium was deposited on three different supports and used to catalyse the reactions.

The objectives include:

1. To study the effect of different supports on light off temperature of rhodium based catalysts,
2. To investigate the reaction mechanism by employing a combined transient-steady state experiments
3. To study of reaction products distribution using different supported rhodium based catalysts.

5.2 Experimental procedure

Three rhodium based catalysts ($\text{Rh}/\text{Al}_2\text{O}_3$, $\text{Rh}/\text{CeO}_2\text{-ZrO}_2$, and $\text{Rh}/\text{CeO}_2/\delta\text{-Al}_2\text{O}_3$) were used in this study. All catalysts were prepared in the laboratory as described in Chapter 4. The apparatus used, catalyst loading and activation testing were described in Chapter 3. The O:C ratio used was explained in detail in Appendix i. Blank runs were performed using only a support ($\alpha\text{-Al}_2\text{O}_3$) at a mild condition (ca. 350 °C) and no activity was observed due to the reactor wall, $\alpha\text{-Al}_2\text{O}_3$, associated tubing, and the pre-heater .

5.3 Results and discussions

The conversion of liquid fuels to hydrogen is usually initiated at temperatures greater than room temperature. This is achieved by combusting part of the fuel [2]. It is necessary to establish the temperature at which combustion becomes significant (light off temperature) and the first objective was to determine this value for isooctane.

5.3.1 Thermodynamic predictions

Initial calculations were carried out to predict the disappearance of reactants and appearance of products based on thermodynamic calculations. Theoretical equilibrium composition based on the adiabatic combustion of octane at room temperature was calculated first, followed by calculation of the effect of temperature on the reaction, using an inlet O:C ratio of 1.56:1.

Calculations were performed with the aid of an Aspen Plus 10.01 steady state simulation package involving the use of the Gibbs reactor icon. In principle, this involves rigorous calculations of reaction and/or multiphase equilibria based on the minimisation of Gibbs free energy. In practice, the expected equilibria may or may not be achieved. Data used with the package includes physical and thermochemical properties of all species. A Peng-Robinson equation of state [12] was chosen as a default value for the oil and gas processing model. Since a data base for isooctane was not available in this version of package, octane was employed as an approximation.

Results are summarised in Table 5.1 and in Figure 5.1. It is clearly seen that oxidation is initiated at 20°C and leads to total oxidation. This value is low compared to experimental measurements (see below).

Steam reforming of methane is predicted to start at temperatures as low as 200°C, again a low prediction. Carbon dioxide reforming is predicted to begin at ca. 400°C.

At 600 °C, the predicted products composition is ca. 6.4 % H₂, 1.5 % H₂O, 4.4 % CO, 3 % CO₂ and ca. 0.2 % CH₄.

Table 5.1 Adiabatic combustion of octane (O:C ratio = 1.56:1)

Inlet Temperature, °C	20	
Outlet Temperature, °C	591	
Species	Feed [mole %]	Product [mole %]
C ₈ H ₁₈	1	0.00
CH ₄	0	0.20
CO	0	4.29
CO ₂	0	2.83
H ₂	0	6.36
O ₂	6.25	0.00
H ₂ O	0	1.49
Inert	92.75	84.84
Total	100	100

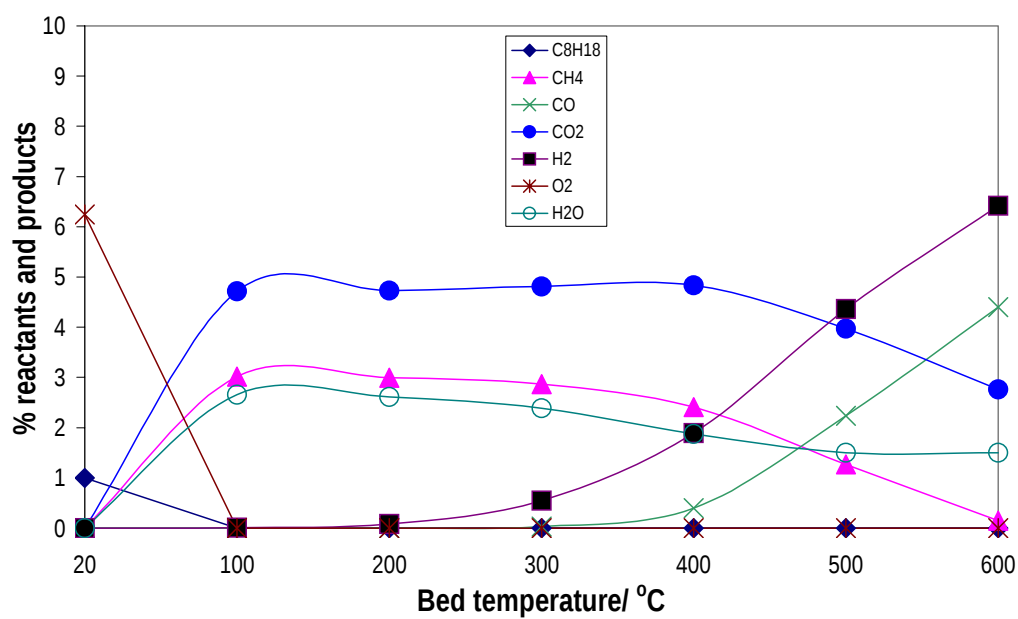


Figure 5.1 Equilibrium reactant and product distribution for partial oxidation of octane (O:C = 1.56:1)

5.3.2 Preliminary testing

A preliminary partial oxidation run was carried out in which a stream of isooctane, oxygen and a diluent gas (O:C ratio 1.56:1) was passed over a pre-reduced Rh/Al₂O₃ catalyst and the temperature was then ramped at 5°C min⁻¹ from room temperature to 600°C (Figure 5.2). Oxidation was initiated at ca. 200°C and all oxygen was consumed by 300°C. Carbon dioxide and water were the only products seen.

Once oxygen had been consumed, steam reforming was observed, carbon monoxide and hydrogen increasing as the temperature increased above 300°C. Methane production was observed above ca. 400°C, suggesting methanation may be of importance : corresponding decreases in carbon monoxide and hydrogen were observed (Figure 5.2).

The observations of this preliminary run were used to plan more detailed studies of the catalysts.

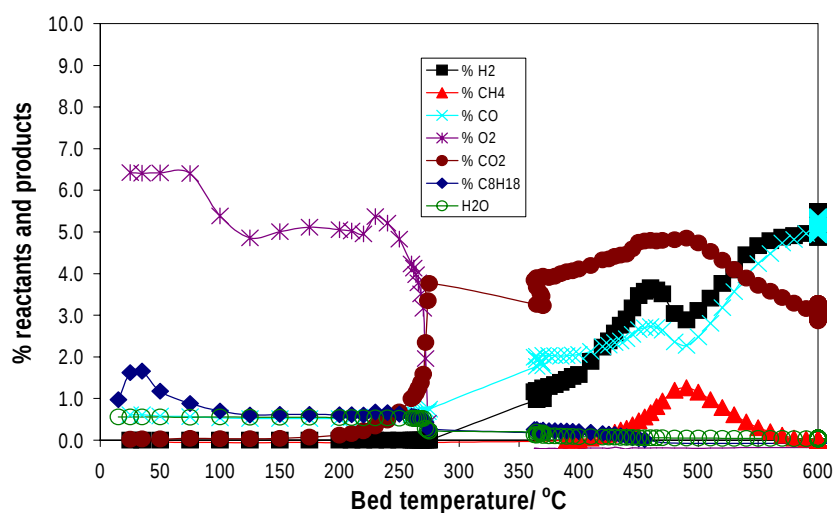


Figure 5.2 A preliminary TPO run (Rh/Al₂O₃ reduced catalyst; GHSV 56400 h⁻¹; inlet i-octane 1 %; weight of catalyst 0.2 g; temperature ramp 5°C min⁻¹; Ar as diluent 187.50 mL min⁻¹; total flow 200 mL min⁻¹; H₂O product uncalibrated)

5.3.3 Rh/Al₂O₃ catalyst

5.3.3.1 Partial oxidation

The disappearance of reactants and the appearance of products were examined as a function of temperature, using a transient-steady state control sequence. Temperature was ramped at ca. 5°C min⁻¹ for ca. 75 min and then held steady until the system stabilised. Measurements were taken (at a real time basis) and temperatures were ramped for another set of experiment.

The reactants showed some interesting trends (Figure 5.3). The inlet isooctane concentration was 1 % but clear evidence of adsorption/concentration/desorption was seen between 25°C and 100°C. At 200°C, the concentration was 1%, dropping dramatically at 210°C to ca 0.5 - 0.6 %. Thus 205°C is a reasonable estimate of light off.

Product analysis (Figure 5.4 A and B) showed that not all of the oxygen was removed till ca. 300°C, but that a small amount of hydrogen was produced between 210°C and 300°C.

At ca. 500 °C, the hydrocarbon was used up.

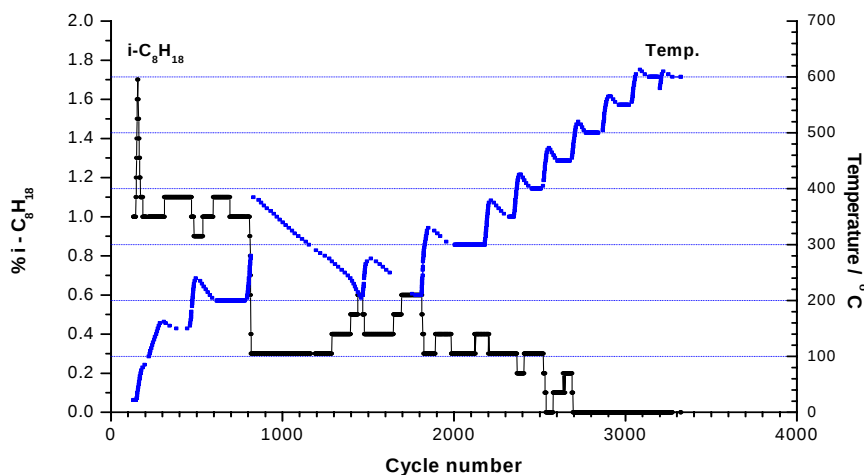


Figure 5.3 Reactant distribution for partial oxidation of isooctane (Rh/Al₂O₃ reduced catalyst 0.2 g; GHSV 56400 h⁻¹; inlet i-octane 1%; O:C ratio 1.56:1; Ar as diluent 187.5 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramp 5°C min⁻¹)

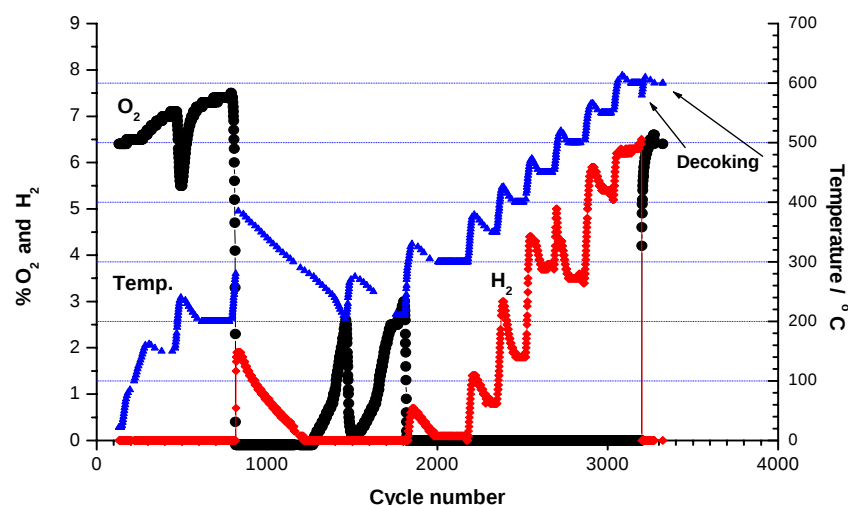


Figure 5.4 A O_2 and H_2 distribution for partial oxidation of isooctane and subsequent decoking test (Rh/Al₂O₃ reduced catalyst 0.2 g; GHSV 56400 h⁻¹; inlet i-octane 1%; O:C ratio 1.56:1; Ar as diluent 187.5 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramp 5 °C min⁻¹; H₂O uncalibrated)

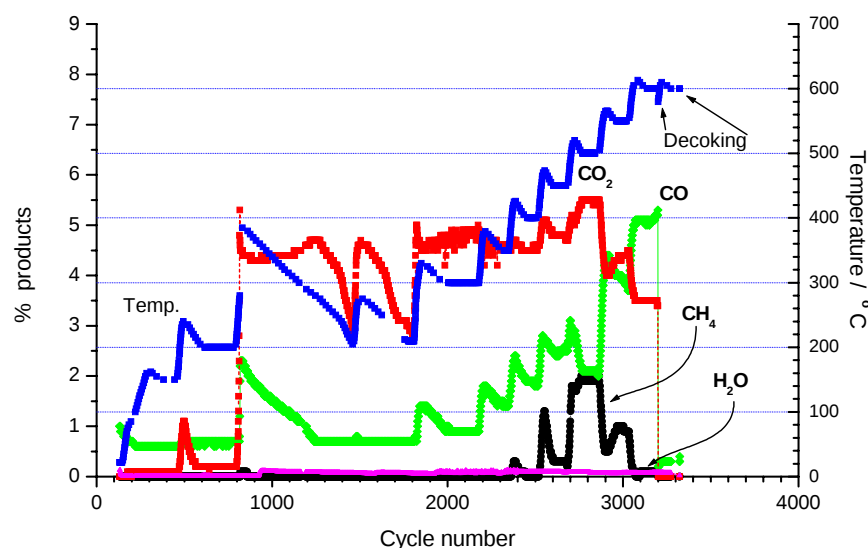


Figure 5.4 B Product distribution for partial oxidation of isooctane and subsequent decoking test (Rh/Al₂O₃ reduced catalyst 0.2 g; GHSV 56400 h⁻¹; inlet i-octane 1%; O:C ratio 1.56:1; Ar as diluent 187.5 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramp 5 °C min⁻¹; H₂O uncalibrated)

Examination of carbon balance at 600 °C revealed no carbon formation since the amount of CO₂ was ca 3.4 % and CO was ca. 5.2 % showing that the total carbon content was about the same as the amount of carbon in isooctane. A subsequent decoking test at

600 °C proved that no carbon was degasified. It should be noted that all decoking experiments were done by passing a diluted oxygen stream (mostly argon unless otherwise stated) of ca. 6 % over a used catalyst at 600°C for 30 min.

5.3.3.2 Methanation and CO₂ reforming

Proof of methanation and CO₂ reforming were demonstrated by separate experiments as shown in Figure 5.5 and Figure 5.7.

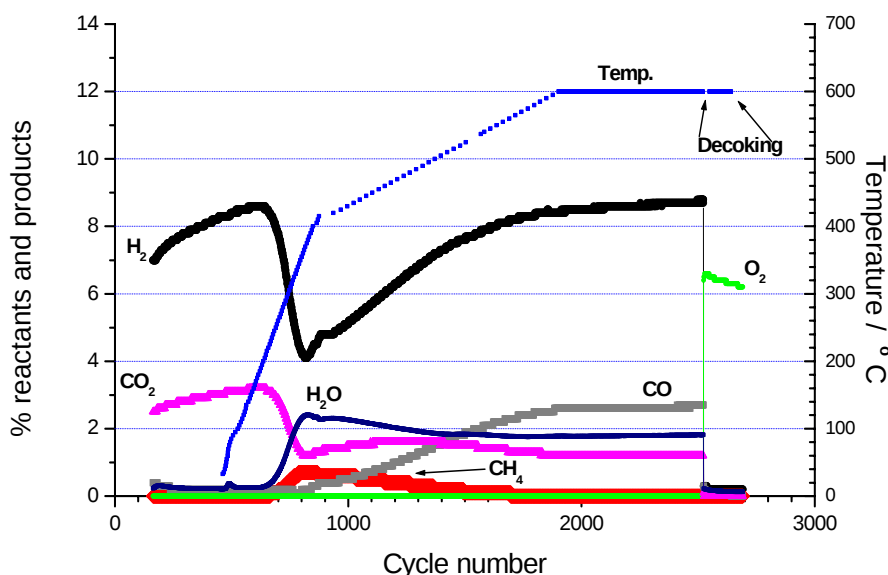


Figure 5.5 Reactant/ product distribution for methanation and subsequent decoking test (Rh/Al₂O₃ reduced catalyst 0.2 g; GHSV 56400 h⁻¹; inlet H₂ 7%; inlet CO₂ 2.5%; Ar as diluent 181 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramps 5 °C min⁻¹ from ambient to 400°C and 1°C min⁻¹ onwards; H₂O uncalibrated)

A methanation run was carried out in which a stream of hydrogen, carbon dioxide (H₂:CO₂ ratio 3:1), and argon as a diluent was passed over a 0.14 g (diluted by 1.3 g of α -Al₂O₃) pre-reduced catalyst and the temperature was then ramped at 5°C min⁻¹ from room temperature to 400°C (Figure 5.5), followed by ramping at 1°C min⁻¹ to 600°C.

Results were presented in Figure 5.5. It was clearly observed that, H_2 increased from an inlet value of 7 % to 8.5 % at the maximum and CO_2 increased from an inlet value of 2.5 % to 3 % before methanation started at ca. 300 °C. This was attributed to the excessive feed gases adsorption/concentration/desorption due to the high surface area of the alumina support during the first period of rapid ramping. Once the system settled down, the ratio of feed gases was the same as at the initial condition.

Under the experimental conditions, the highest amount of CH_4 produced was only ca. 0.5 % at 300 °C, which was far from the expected equilibria of ca. 1.5 % (Figure 5.6). At 600 °C, CH_4 was converted by steam and carbon dioxide reforming. The residual CO_2 concentration (ca.1%) was similar to the predicted equilibrium calculation. The thermodynamic calculations were undertaken with the aid of the same simulation package as was previously described. Decoking tests at the end of experimental run exhibited no carbon removal.

A CO_2 reforming run was also performed, in which a stoichiometric ratio of 1% isooctane to 8 % of CO_2 was passed over a pre-reduced catalyst and a similar temperature control sequence to the methanation experiment was applied (Figure 5.7).

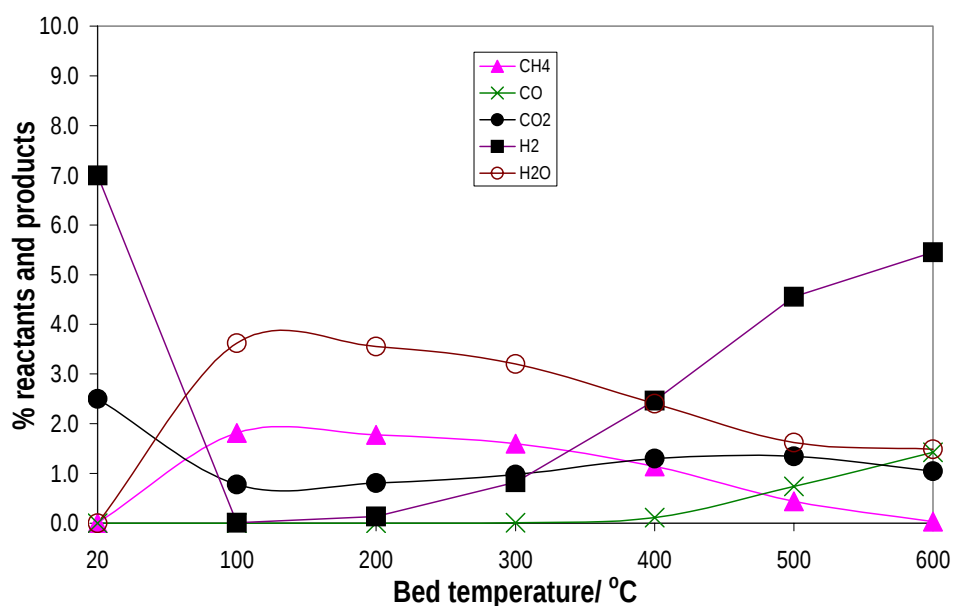


Figure 5.6 Equilibrium reactant/product distribution for methanation ($\text{H}_2:\text{CO}_2 = 3:1$)

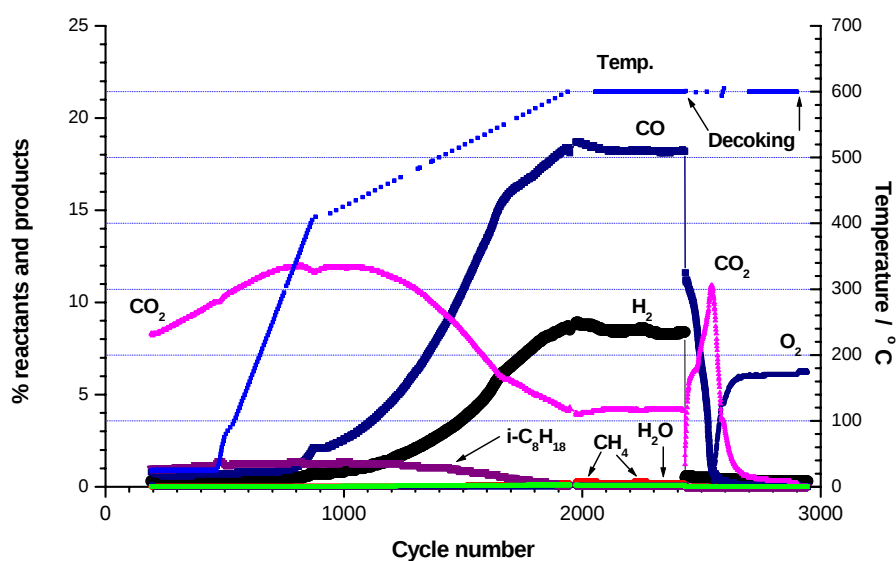


Figure 5.7 Reactant/ product distribution for CO_2 reforming of isooctane and subsequent decoking test (Rh/ Al_2O_3 reduced catalyst 0.2 g; GHSV 56400 h^{-1} ; inlet i-octane 1%; inlet CO_2 8%; Ar as diluent 182 mL min^{-1} ; total flow 200 mL min^{-1} ; temperature ramps 5 $^\circ\text{C min}^{-1}$ from ambient to 400 $^\circ\text{C}$ and 1 $^\circ\text{C min}^{-1}$ onwards; H_2O uncalibrated)

It was clearly observed that adsorption/concentration/desorption of carbon dioxide was evident at the fast temperature ramping region up to ca. 400 $^\circ\text{C}$. H_2 production hit the

highest level of ca. 9 % at 600 °C. There was an indication of carbon formation since a clear CO₂ peak occurred during decoking. The deposited carbon was completely burned by an oxygen stream within a short period of time.

5.3.4 Rh/CeO₂-ZrO₂

5.3.4.1 Partial oxidation experiment

The first experiment was carried out by raising the temperature from ca. 25 °C to 600 °C. Steady state runs involved controlling the reactor at 210 °C, 250 °C, 300 °C, 400 °C, 500 °C, and 600 °C for about 30 minutes at each temperature. The results are presented in Figure 5.8, associated with Figure 5.9 A and B.

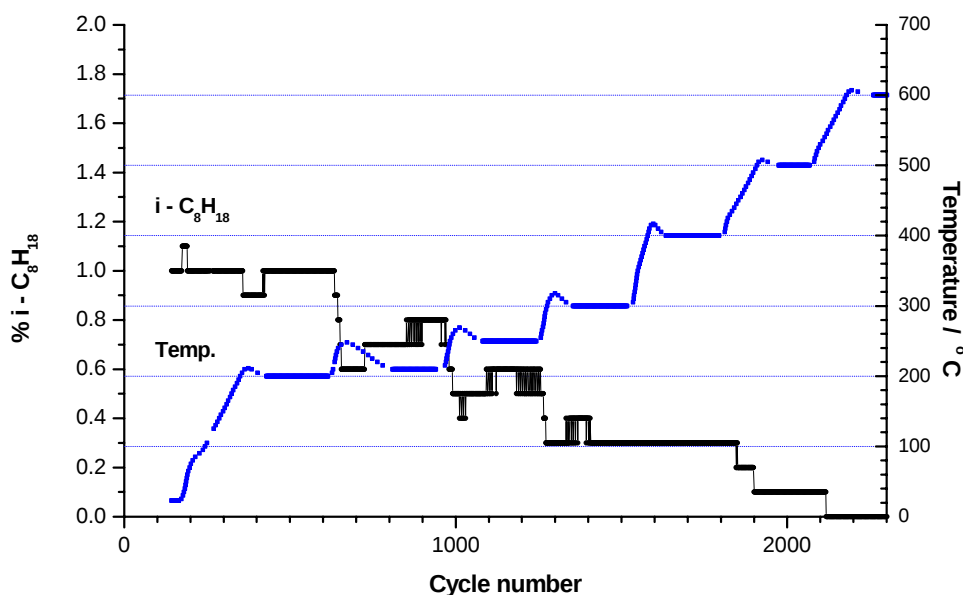


Figure 5.8 Reactant distribution for partial oxidation of isooctane (Rh/CeO₂-ZrO₂ reduced catalyst 0.2 g; GHSV 54000 h⁻¹; inlet i-octane 1%; O:C ratio 1.56:1; Ar as diluent 187.5 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramp 5°C min⁻¹)

From Figure 5.8, it is observed that the initial hydrocarbon desorption at low temperature is much weaker than that of alumina support (Section 5.3.3). Isooctane lights off at about 210 °C and is completely consumed at above 500 °C. O₂ is used up by 300 °C, while H₂ is detected at 300 °C (Figure 5.9 A). CO₂ reforming occurred between 450 °C - 500 °C and interestingly, no CH₄ is detected at all temperatures (Figure 5.9 B). At 600°C the ratio of H₂/CO is 1.44 or very close to the ratio predicted by equilibrium calculation of 1.45 (Figure 5.1). However, it is not clear whether H₂ and O₂ can co-exist before O₂ is used-up.

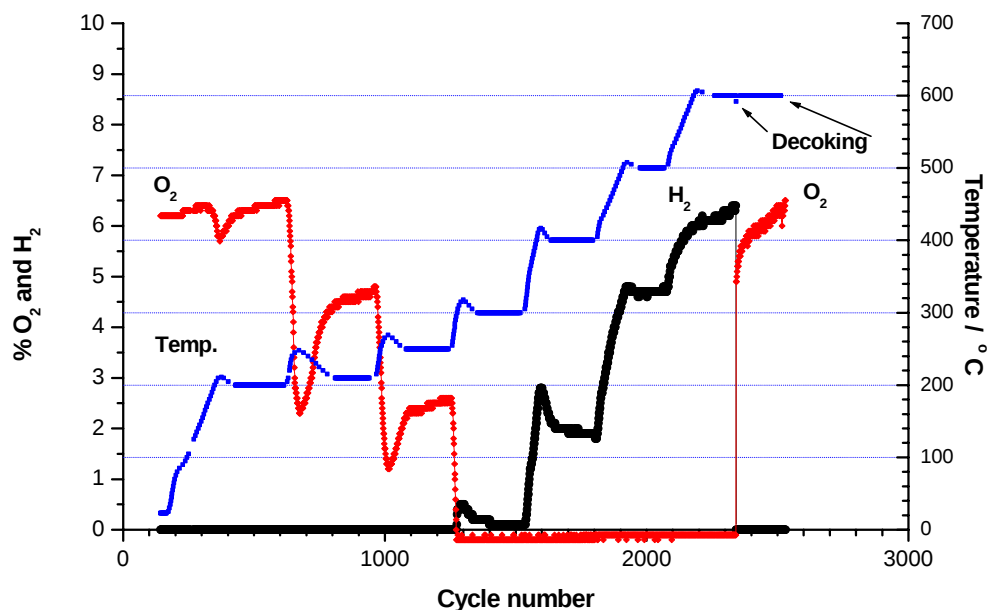


Figure 5.9 A O_2 and H_2 distribution for partial oxidation of isooctane and subsequent decoking test (Rh/CeO₂-ZrO₂ reduced catalyst 0.2 g; GHSV 54000 h⁻¹; inlet i-octane 1%; O:C ratio 1.56:1; Ar as diluent 187.5 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramp 5 °C min⁻¹)

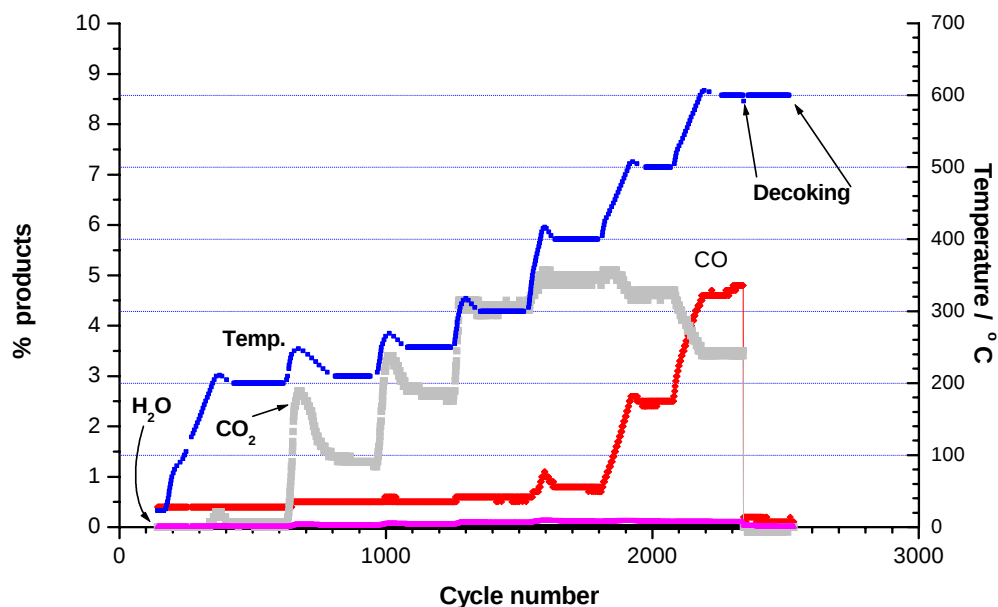


Figure 5.9 B Product distribution for partial oxidation of isooctane and subsequent decoking test (Rh/CeO₂-ZrO₂ reduced catalyst 0.2 g; GHSV 54000 h⁻¹; inlet i-octane 1%; O:C ratio 1.56:1; Ar as diluent 187.5 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramp 5 °C min⁻¹; H₂O uncalibrated)

A second experiment was then performed and the steady-state runs were increased from 260 °C to 300 °C at 10 °C interval, and then continued at 450 °C, 550 °C, 575 °C, and 600 °C respectively. As can be seen in Figure 5.10, isooctane was totally consumed at above ca. 500°C. From Figure 5.11 A, it was evident that H₂ and O₂ co-existence occurred at ca. 280 °C - 290 °C and that the O₂ reproducibly disappeared at 300 °C. There was no occurrence of CH₄ but CO₂ reforming was observed at above ca. 450 °C. Both catalysts were subjected to decoking at 600 °C and no carbon formation was detected (Figure 5.11 B).

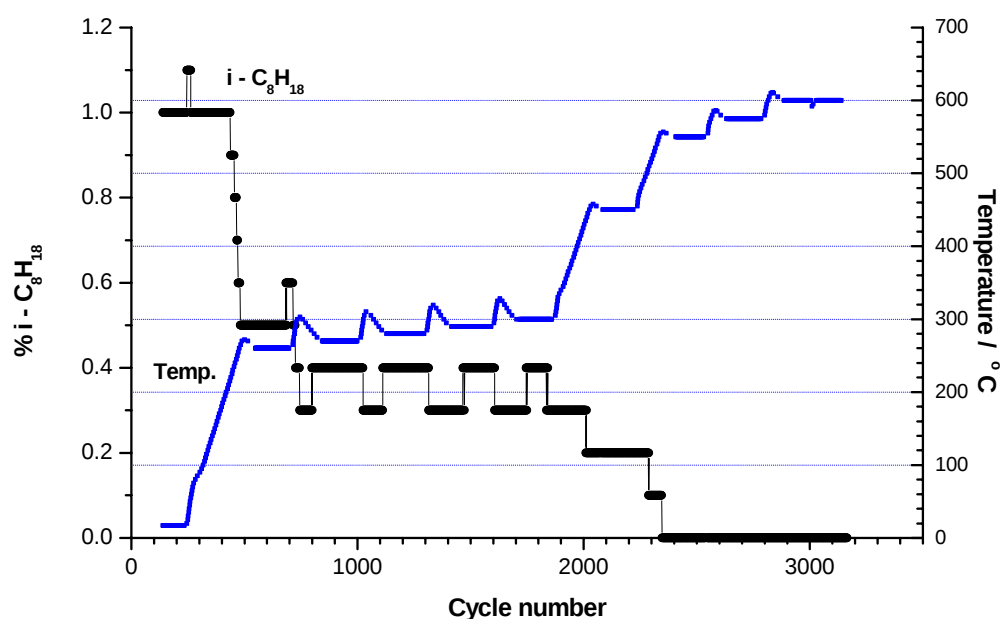


Figure 5.10 Reactant distribution for partial oxidation of isooctane and subsequent decoking test (2nd run, Rh/CeO₂-ZrO₂ reduced catalyst 0.2 g; GHSV 54000 h⁻¹; inlet i-octane 1%; O:C ratio 1.56:1; Ar as diluent 187.5 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramp 5 °C min⁻¹; H₂O uncalibrated)

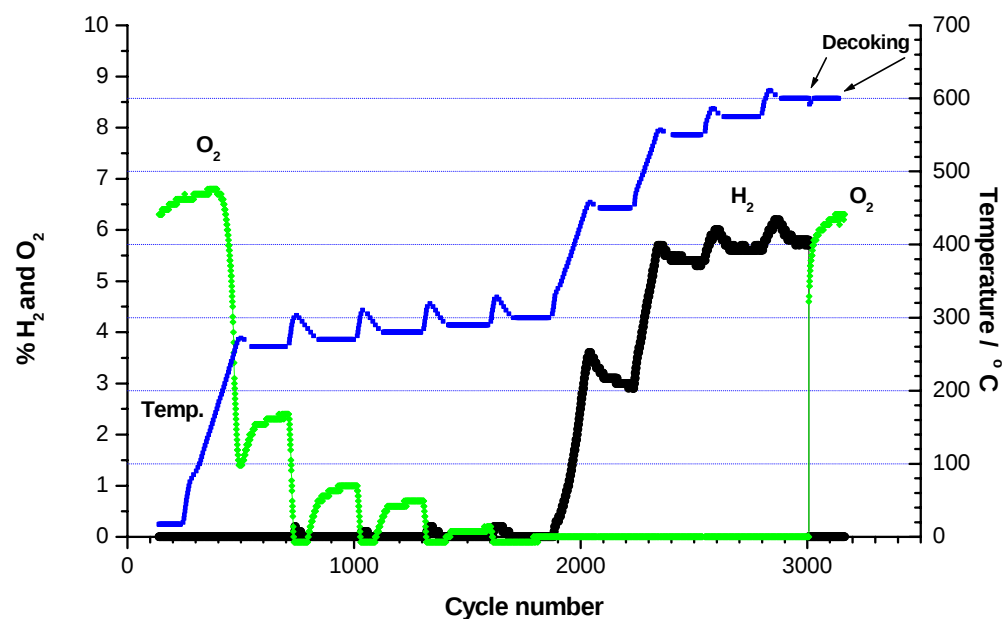


Figure 5.11 A O_2 and H_2 distribution for partial oxidation of isooctane and subsequent decoking test (2nd run, Rh/CeO₂-ZrO₂ reduced catalyst 0.2 g; GHSV 54000 h⁻¹; inlet i-octane 1%; O:C ratio 1.56:1; Ar as diluent 187.5 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramp 5 °C min⁻¹)

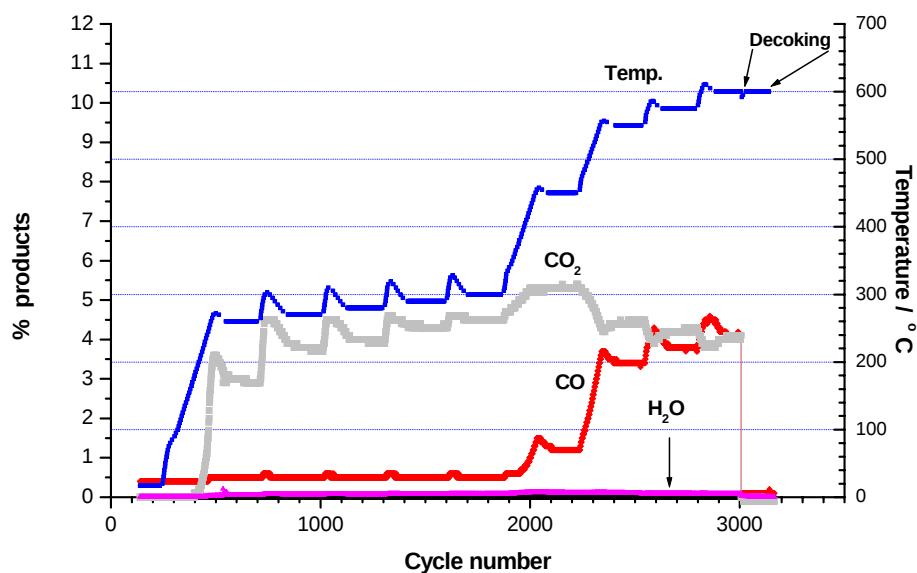


Figure 5.11 B Product distribution for partial oxidation of isooctane and subsequent decoking test (2nd run, Rh/CeO₂-ZrO₂ reduced catalyst 0.2 g; GHSV 54000 h⁻¹; inlet i-octane 1%; O:C ratio 1.56:1; Ar as diluent 187.5 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramp 5 °C min⁻¹; H₂O uncalibrated)

5.3.4.2 Steam reforming experiment

From partial oxidation runs, it was known that steam reforming was initiated when ca. 60 % of hydrocarbon feed was converted into CO_2 and H_2O . Therefore, it was intended to confirm the finding by performing a steam reforming run. A steam/carbon ratio of 2 was chosen [13], and a transient control sequence was undertaken by ramping the operating temperature from ambient to 400 °C at 5 °C min⁻¹ and consecutively from 400 °C to 600 °C at 1 °C min⁻¹.

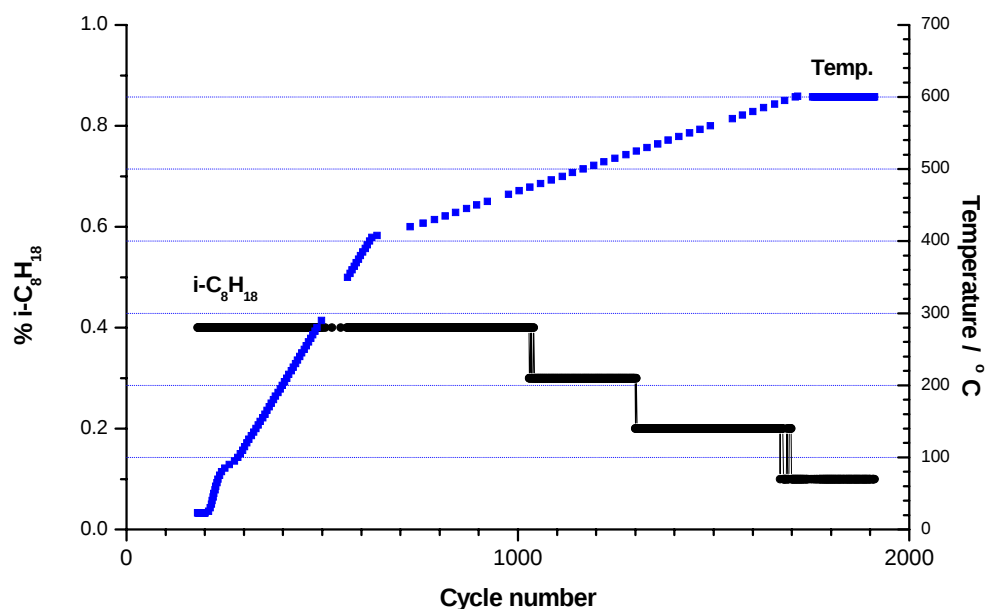


Figure 5.12 Reactant distribution for steam reforming of isooctane and subsequent decoking test (Rh/CeO₂-ZrO₂ reduced catalyst 0.2 g; GHSV 54000 h⁻¹; inlet i-octane 0.4%; S:C ratio 2:1; Ar as diluent 186.4 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramp 5 °C min⁻¹; H₂O calibrated)

Steam reforming started at above ca. 400°C and complete conversion of isooctane was not observed even at 600°C as illustrated by Figure 5.12. It was not surprising, since this particular endothermic reaction was thermodynamically controlled.

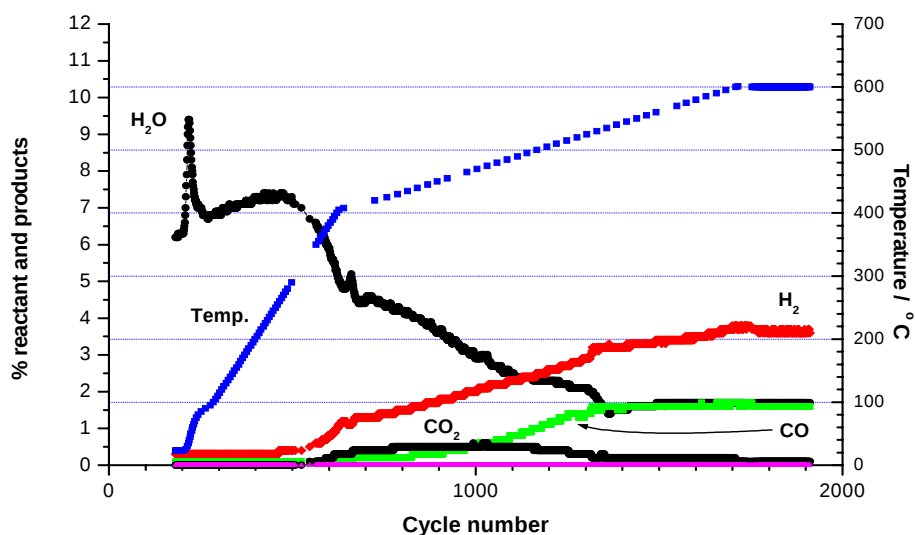


Figure 5.13 A Reactant/product distribution for steam reforming of isooctane and subsequent decoking test (Rh/CeO₂-ZrO₂ reduced catalyst 0.2 g; GHSV 54000 h⁻¹; inlet i-octane 0.4%; S:C ratio 2:1; Ar as diluent 186.4 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramp 5 °C min⁻¹; H₂O calibrated)

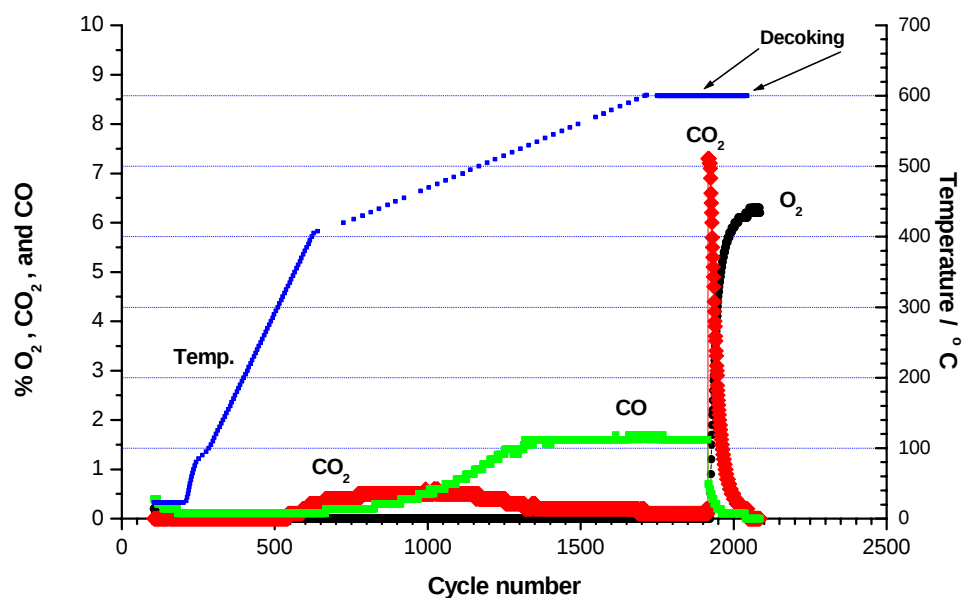


Figure 5.13 B O₂, CO₂, and CO distribution for steam reforming of isooctane and subsequent decoking test (Rh/CeO₂-ZrO₂ reduced catalyst 0.2 g; GHSV 54000 h⁻¹; inlet i-octane 0.4%; S:C ratio 2:1; Ar as diluent 186.4 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramp 5 °C min⁻¹; H₂O calibrated)

It was clear from Figure 5.13 A, that H₂O desorbed at ca. 150 °C - 200 °C before attaining the determined concentration of ca. 7 %. Rapid consumption of H₂O was initiated at ca. 400 °C which was then simultaneously followed by H₂, CO, and CO₂ production. CO₂ reforming occurred at about 500 °C and this corresponded to an increase of H₂. No CH₄ was detected. At 600 °C, the main products were 3.5 % H₂ and 1.5% CO, with CO₂ being less than 0.5 %. The product distribution was less than that predicted by equilibrium calculation except for CO, as shown by Figure 5.14 . Carbon balance calculation indicated some sort of carbon formation and this was confirmed by a decoking run, where CO₂ overshoot was evident (Figure 5.13 B).

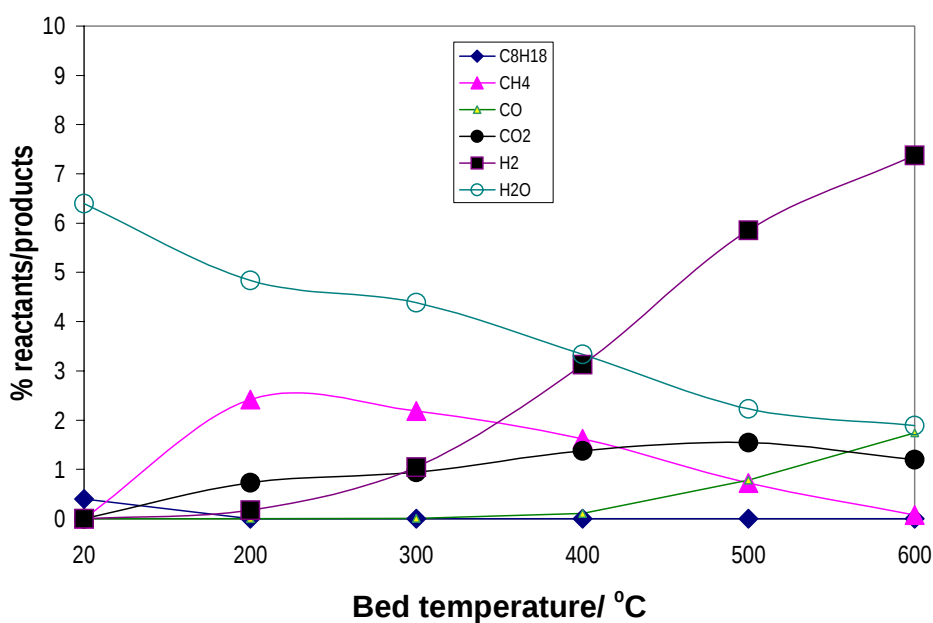


Figure 5.14 Equilibrium reactant/product distribution for steam reforming of isooctane (S:C ratio 2:1)

5.3.4.3 CO₂ reforming

CO₂ reforming was also confirmed by undertaking a transient run under the same conditions as steam reforming. As depicted by Figure 5.15, at ca. 520 °C - 540 °C hydrocarbon light out (the temperature at which CO₂ reforming starts to take place) was attained, but complete consumption of isooctane was not achieved even at 600 °C. This was also not surprising in the context of a thermodynamically controlled reaction. Based on the reaction (5.5),



the ratio of CO/H₂ products at maximum conversion should be 1.8 and at 600 °C (where a steady state control sequence was experimentally maintained), this particular ratio was 1.9 as illustrated by Figure 5.16. This was quite close to the maximum predicted ratio.

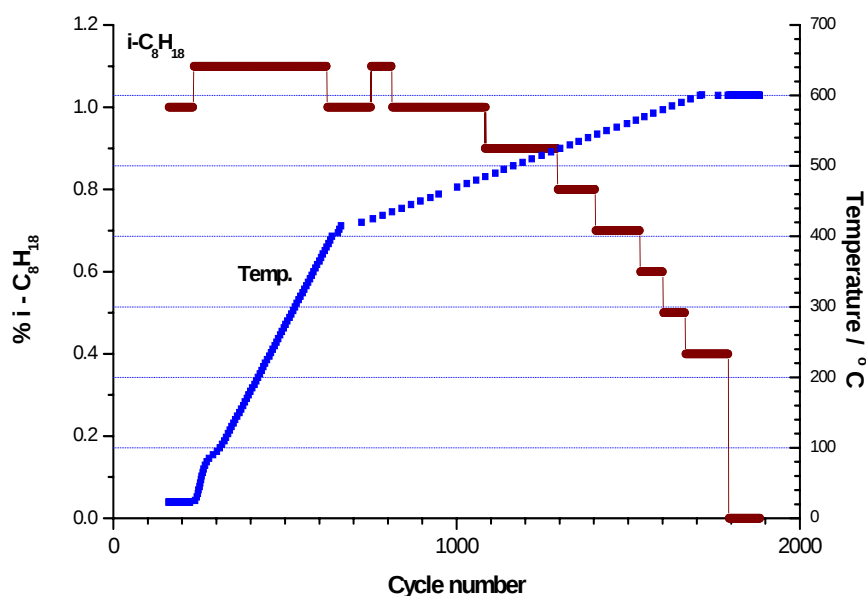


Figure 5.15 Reactant distribution for CO₂ reforming of isooctane and subsequent decoking test (Rh/CeO₂-ZrO₂ reduced catalyst 0.2 g; GHSV 54000 h⁻¹; inlet i-octane 1%; inlet CO₂ 8%; Ar as diluent 182 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramps 5 °C min⁻¹ from ambient to 400°C and 1°C min⁻¹ onwards; H₂O uncalibrated)

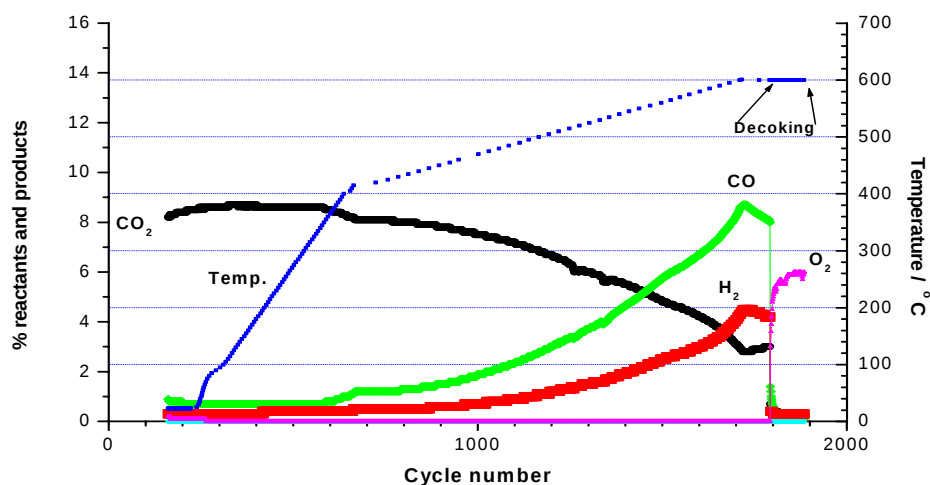


Figure 5.16 Reactant/product distribution for CO₂ reforming of isooctane and subsequent decoking test (Rh/CeO₂-ZrO₂ reduced catalyst 0.2 g; GHSV 54000 h⁻¹; inlet i-octane 1%; inlet CO₂ 8%; Ar as diluent 182 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramps 5 °C min⁻¹ from ambient to 400°C and 1°C min⁻¹ onwards; H₂O uncalibrated)

It is interesting to note that there was no CH₄ produced and, concomitantly, the amount of residual CO₂ was about 3 % (Figure 5.16) or almost three fold the equilibrium value of 1.2 % (Table 5.2, calculated with the aid of an Aspen Plus 10.01). Therefore the finding suggested that the methanation was unfavourable with this particular catalyst support and this was in agreement with the results of the partial oxidation experiment. Decoking tests at 600 °C proved that there was no carbon formation.

Table 5.2 The expected equilibria of CO₂ reforming of isooctane at 600°C (inlet i-C₈H₁₈ 1%; i-C₈H₁₈ / CO₂ ratio 1 : 8)

Species	Mole %
i-C ₈ H ₁₈	0.00
CH ₄	1.41
CO	11.56
CO ₂	1.22
H ₂	4.96
H ₂ O	0.19
Inert	80.66

5.3.5 Rh/CeO₂/δ-Al₂O₃ catalyst

The last experiment to study the influence of catalyst supports on light off temperature and products distribution is summarised in Figure 5.17 and Figure 5.18.

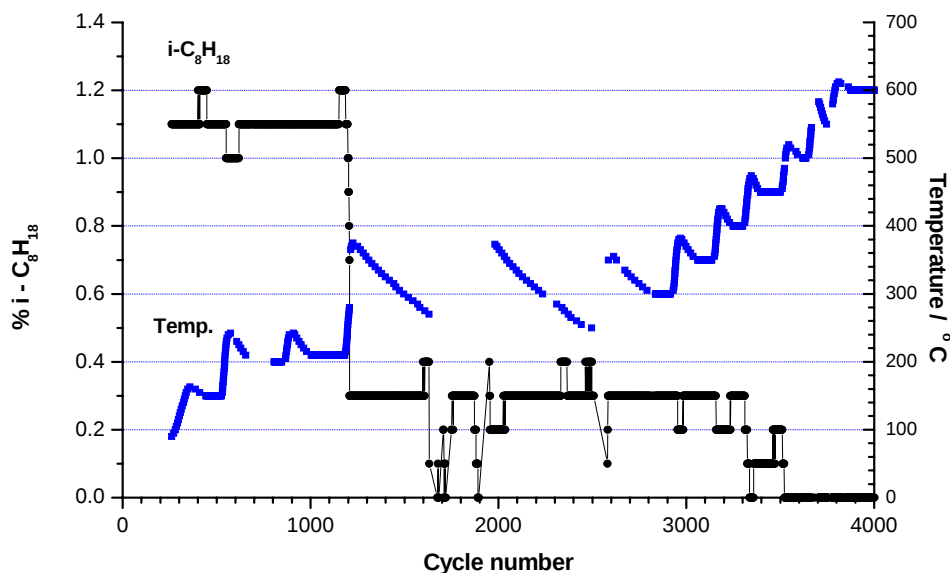


Figure 5.17 Reactant distribution for partial oxidation of isooctane and subsequent decoking test (Rh/CeO₂/δ-Al₂O₃ reduced catalyst 0.2 g; GHSV 34200 h⁻¹; inlet i-octane 1%; O:C ratio 1.56:1; Ar as diluent 187.5 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramp 5 °C min⁻¹; H₂O uncalibrated)

The hydrocarbon was desorbed at a lower temperature and stabilised at 1% ± 0.1 at 210°C. During the subsequent temperature ramp, the isooctane supply became disconnected. The reactor was cooled to 220°C and the isooctane brought back on line. The exit concentration was found to be ca. 0.3 %, showing the light-off temperature to be between 210°C - 220°C. Isooctane was completely consumed at 500 °C.

Oxygen was used-up at 300 °C as may be seen from Figure 5.18 A, and methanation was initiated at ca. 400 °C - 450 °C (Figure 5.18 B). The methane highest peak of 2 % was attained at 500 °C. However, it was completely converted to H₂ as well as carbon-oxides at 600 °C (Figure 5.18 B). The existence of methanation was also tested in a separate run

(Figure 5.19) and this graph also displays evidence of CH_4 removal by steam and CO_2 reforming. Decoking tests at 600 °C after the partial oxidation run showed that there was no carbon formation (Figure 5.19 at cycle 2000 on wards)

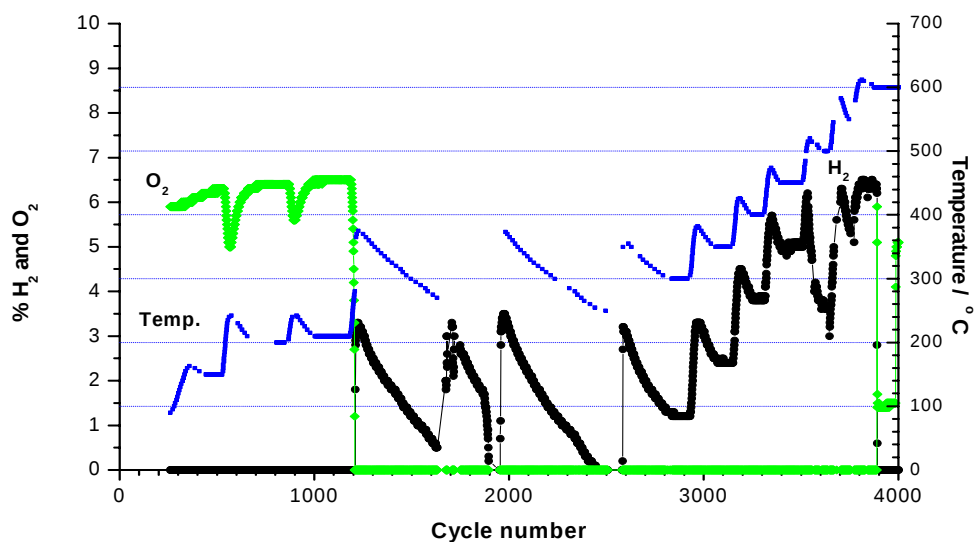


Figure 5.18 A H_2 and O_2 distribution for partial oxidation of isooctane and subsequent decoking test (Rh/CeO₂/δ-Al₂O₃ reduced catalyst 0.2 g; GHSV 34200 h⁻¹; inlet i-octane 1%; O:C ratio 1.56:1; Ar as diluent 187.5 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramp 5 °C min⁻¹; H₂O uncalibrated)

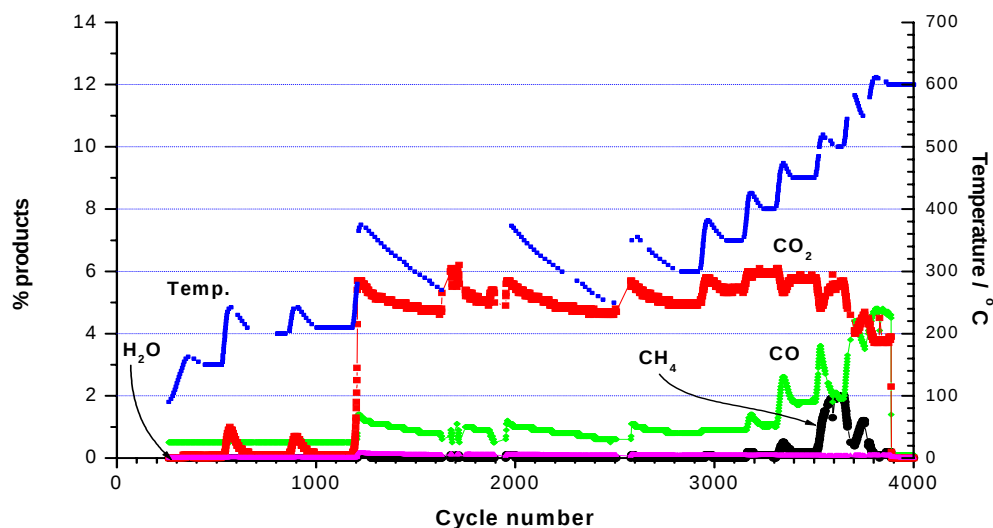


Figure 5.18 B Product distribution for partial oxidation of isooctane and subsequent decoking test (Rh/CeO₂/δ-Al₂O₃ reduced catalyst 0.2 g; GHSV 34200 h⁻¹; inlet i-octane 1%; O:C ratio 1.56:1; Ar as diluent 187.5 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramp 5 °C min⁻¹; H₂O uncalibrated)

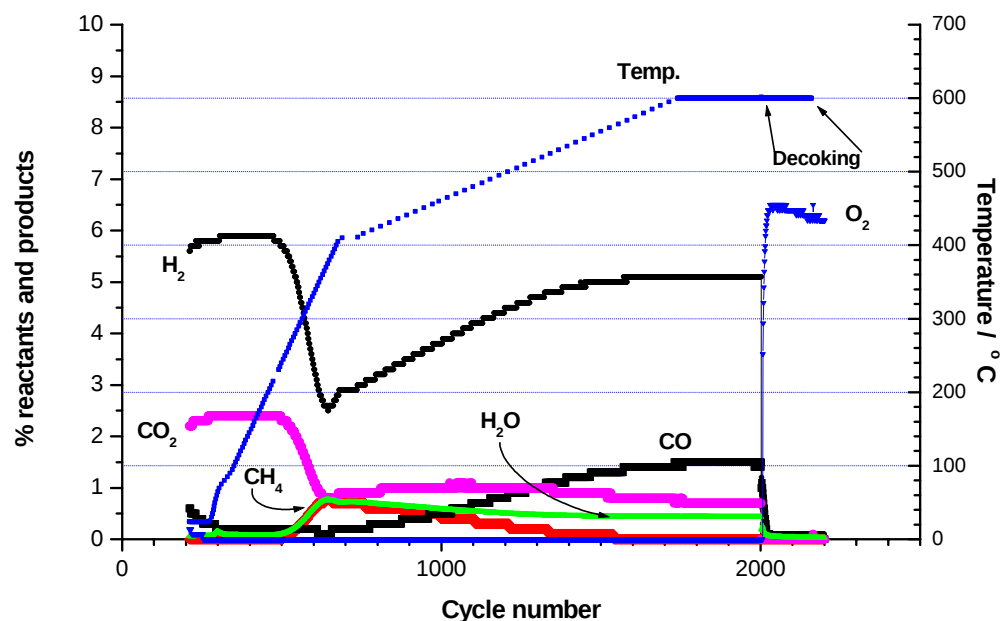


Figure 5.19 Reactant/product distribution for methanation and subsequent decoking test (Rh/ CeO₂/δ-Al₂O₃ reduced catalyst 0.2 g; GHSV 34200 h⁻¹; inlet H₂ 7%; inlet CO₂ 2.5%; Ar as diluent 181 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramps 5 °C min⁻¹ from ambient to 400°C and 1°C min⁻¹ onwards; H₂O uncalibrated)

5.3.6 Influence of support on the light off temperature of isooctane

Figure 5.20 summarises the effect of three different supports on the isooctane light off temperature for rhodium based catalysts. Obviously, oxidation begins at 200 °C - 220 °C irrespective of the kind of support. Two reaction regions are observed. Firstly, between 200 °C - 300 °C, isooctane total oxidation increases rapidly and tends to stabilise at about 60 % conversion. Secondly, at temperature higher than 300 °C, isooctane conversion increases again at a slower rate towards complete conversion at ca. 500 °C.

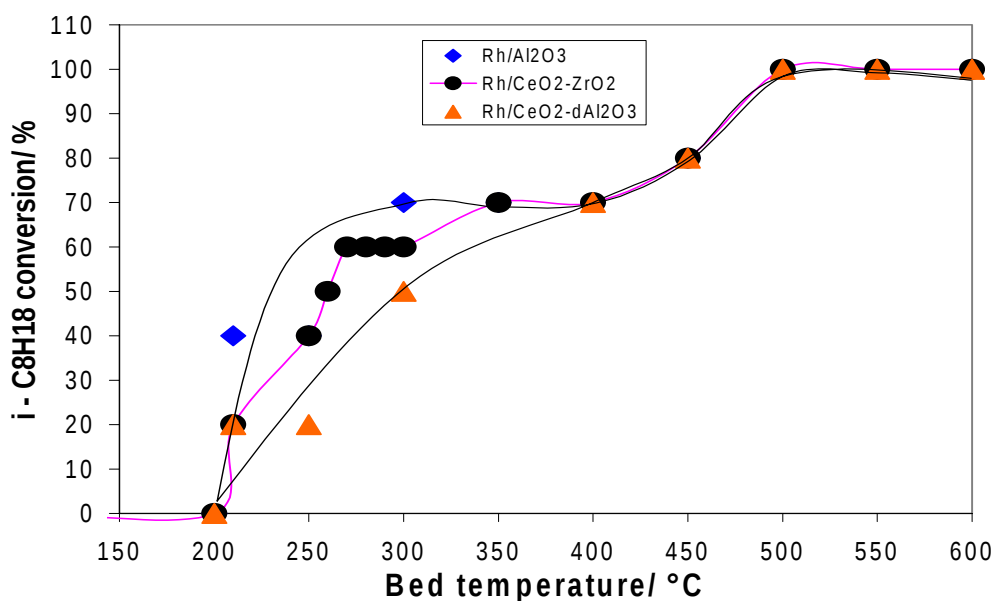


Figure 5.20 Support effect towards partial oxidation of isooctane (various reduced catalysts 0.2 g; GHSV 34200 – 56400 h⁻¹; inlet i-octane 1%; O:C ratio 1.56:1; Ar as diluent 187.5 mL min⁻¹; total flow 200 mL min⁻¹)

5.3.7 Evidence of indirect partial oxidation of isooctane

Some explanation of indirect partial oxidation of isooctane were obtained by measuring oxygen consumption and hydrogen production. Figure 5.21 shows hydrogen formation as well as oxygen consumption over Rh/CeO₂-ZrO₂. This graph is extracted from previous Rh/CeO₂-ZrO₂ plots. In the first reaction zone, O₂ is gradually consumed and is used-up at 300 °C. However, H₂ is produced significantly at temperature above 300 °C despite the fact that a small amount of H₂ can co-exist at lower temperatures than 300 °C. Therefore, H₂ is formed by steam reforming of reaction (5.3) or (5.6) as well as by complementary CO₂ reforming of reaction (5.5) rather than by direct oxidation (reaction (5.2) or (5.7)). H₂O and CO₂ produced by total oxidation of reaction (5.1) may be involved in the reactions.



As has been reported by Barbier and Duprez [14], steam reforming at higher than 450°C produces almost exclusively CO as illustrated by equation (5.3). However, for all catalysts, the H₂/CO ratio of ca. 1.8 - 1.9 is very close to the ratio of 2.1 rather than 1.1 as predicted by equation (5.2). A ratio of 2 : 1, is achieved only in a relatively narrow window between 450°C < T < 550°C, above which the ratio tends to decrease even down to 1.3 - 1.4 at 600°C. This fact further supports the concept that the reaction sequences involve total oxidation followed by steam reforming as well as complementary CO₂ reforming. This concept was also proved by the additional CO₂ reforming runs described in the previous sections.

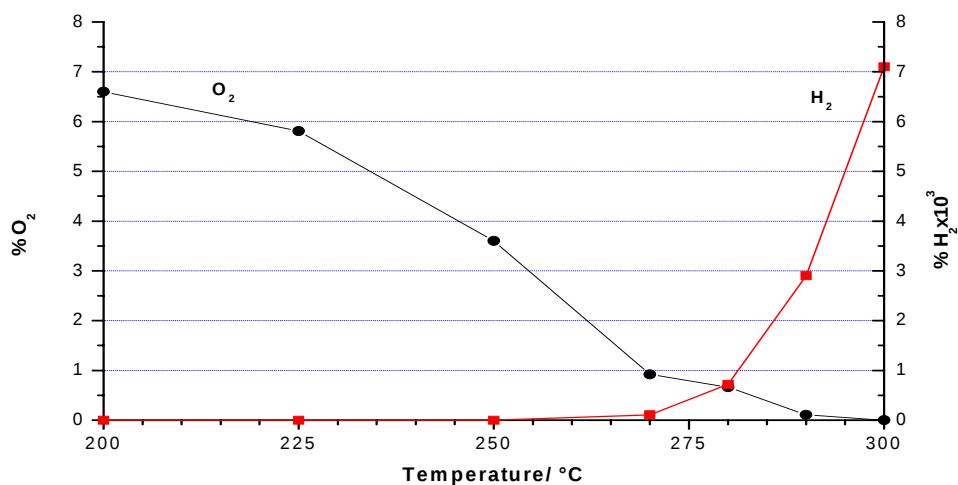


Figure 5.21 H₂ formation and O₂ consumption at lower temperature for partial oxidation of isooctane (Rh/CeO₂-ZrO₂ reduced catalyst 0.2 g; GHSV 54000 h⁻¹; inlet i-octane 1%; O:C ratio 1.56:1; Ar as diluent 187.5 mL min⁻¹; total flow 200 mL min⁻¹; temperature ramp 5°C min⁻¹)

5.3.8 H₂ yield

H₂ yield is defined as the ratio of H₂ produced by partial oxidation reaction divided by H₂ predicted from thermodynamic calculations times 100 %. The results are summarised in Table 5.3.

Table 5.3 Influence on H₂ yield by different supports

Support	Al ₂ O ₃	CeO ₂ - Al ₂ O ₃	CeO ₂ -ZrO ₂
H ₂ produced @ 500 °C, % *)	3.5	3.6	4.6
H ₂ yield @ 500 °C, %	88	90	100
H ₂ produced @ 600°C, %	6.4	6.5	6.5
H ₂ yield @ 600 °C, %	100	100	100

*) Uncertainty $\pm$ 5% (relative)

It is seen that there is no different H₂ yield among three supports at 600 °C, but CO produced by Rh/Al₂O₃ (Figure 5.4 B) is significantly different from either Rh/CeO₂-ZrO₂ (Figure 5.9 B) or Rh/CeO₂-Al₂O₃ (Figure 5.18 B). At 500 °C, the mixed oxide support of CeO₂-ZrO₂ gives much better yield due to the fact that the later support does not favour methanation. To explain this interesting phenomenon, products distribution ratios are presented in Table 5.4 as a basis for discussion.

Table 5.4 Products distribution ratio*)

Catalyst	Rh/Al ₂ O ₃				Rh/CeO ₂ - d Al ₂ O ₃				Rh/CeO ₂ - ZrO ₂			
Temperature, °C	400	450	500	600	400	450	500	600	400	450	500	600
H ₂ /CO	1.0	1.4	1.7	1.2	3.7	2.8	1.8	1.4	2.6	2.2	1.9	1.4
CO/CO ₂	0.4	0.6	0.4	1.5	0.2	0.3	0.4	1.4	0.1	0.3	0.6	1.3
CH ₄ /CO ₂	0	0.06	0.4	0	0	0.04	0.4	0	0	0	0	0
H ₂ yield , %	42	-	88	100	77	-	90	100	40	-	100	100

*)Uncertainty $\pm$ 5% (relative)

The experimental values of the H₂ /CO ratio at higher temperatures (ca. above 450 °C) were found to lie in the range 1.8 – 1.9, which is close to the ratio of 2.1 predicted from equation (5.3) and very different from a ratio of 1.1 predicted from equation (5.2). Thus, it would seem that hydrogen is produced by a combination of total oxidation and reforming, rather than by direct partial oxidation.

The product spectrum showed some interesting trends at higher temperatures. Above ca. 450 °C, methane was observed over some catalysts and distinct changes were observed in the carbon monoxide/carbon dioxide ratio. The hydrogen yield at 400, 500, and 600 °C, defined as the amount observed as a percentage of that expected on the basis of the thermodynamics of reaction (5.2) was also found to vary with the nature of the support.

From Table 5.4, it is evident that for all three catalysts, the stoichiometric ratio, CO/CO_2 , increases with temperature indicating that CO_2 produced during total oxidation was later consumed, most likely via CO_2 dry reforming of the remaining isooctane. Although ceria is a good WGS catalyst, since the CO/CO_2 ratio in WGS is 1, this reaction would not be responsible for the trend observed. However the influence of ceria (which has high adsorption capacity for H_2O) is evident in the H_2/CO ratio. The two catalysts containing ceria displayed a higher H_2/CO ratio at all temperatures, suggesting greater steam reforming activity. Even so, this activity drops with temperature due to the contribution of CO from dry reforming. Indeed both steam and dry reforming appeared to contribute evenly to the overall H_2 and CO production especially at 600°C .

Stoichiometrically, the H_2/CO ratio from steam reforming is about 2.1 while that from dry reforming is about 0.6. It would seem that as temperature increased, dry reforming gained prominence. However, the presence of ceria seemed to give greater weight to steam reforming. Consistent with this, when ceria was absent (as in the $\text{Rh}/\text{Al}_2\text{O}_3$ catalyst) dry reforming contributed more significantly to overall H_2/CO as may be evident from a value of 1 seen for this catalyst.

Interestingly, CH_4 was produced only at 500°C and on $\text{Rh}/\text{Al}_2\text{O}_3$ and $\text{Rh}/\text{CeO}_2\text{-}\delta\text{Al}_2\text{O}_3$ indicating that the ZrO_2 support does not enhance methanation. This is probably due to the fact that alumina support shows better hydrogenation activity than zirconia as previously observed [15, 16].

The product distribution data (Table 5.4) indeed show the appearance of CH_4 in the product stream over $\text{Rh}/\text{Al}_2\text{O}_3$ and $\text{Rh}/\text{CeO}_2\text{-}\delta\text{Al}_2\text{O}_3$ from about 450°C which then

disappeared at 600°C probably due to steam reforming. This explanation is further supported by transient mass spectrometer data (Figure 5.2) which show a peak in CH₄ production precisely at the minima of H₂ and CO curves i.e. CH₄ arises from the CO-H₂ reaction.

5.4 Conclusions

1. All supported Rh based catalysts give a clear picture that the partial oxidation of isooctane is an indirect process. Firstly hydrocarbon is converted into CO₂ and H₂O by total oxidation and, then the remaining feed is further steam reformed as well as CO₂ reformed to produce H₂ and carbon oxides.
2. The three supports being investigated give more or less the same light off temperature of 210 ± 10 °C.
3. Oxygen is totally consumed at 300 °C for the O:C range considered.
4. CeO₂-ZrO₂ solid solution exhibits a better hydrogen selectivity at 500 °C since this particular support does not favour methanation

5.5 References

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Chapter 6 Partial oxidation of artificial gasoline

6.1 Introduction

Hydrogen production by steam reforming of hydrocarbons is an endothermic process which requires an external supply of energy, while catalytic combustion of hydrocarbons produces heat. This has led to the concept of autothermal steam reforming, by which part of the fuel is oxidised to produce heat and part is steam reformed to produce hydrogen. The autothermal reforming of methane [1], methanol [2, 3] and light hydrocarbons [4] has been reported.

The first question for the production of hydrogen by catalytic autothermal reforming of gasoline-like hydrocarbons involves the choice of active metal to catalyse oxidation reactions. Platinum-based catalysts were found more active and stable than nickel-based catalysts in oxidising light hydrocarbons [1]. Recent studies also revealed that platinum was more active than rhodium for the oxidation of aromatics and isooctane, but these reactions were severely inhibited by carbon monoxide [5, 6].

In the context of light hydrocarbons steam reforming, nickel catalysts were found to be superior to platinum based catalysts [1]. Moreover, Ni based-catalysts are widely used for naphtha steam reforming [1, 7-12]. It is therefore expected that Pt-based catalysts will be good candidates for catalytic oxidation of higher hydrocarbons, while Ni-based catalysts will be preferred for steam reforming.

The second question involves the design of the catalyst bed configuration in order to minimise the resistance of both heat and mass transfer. Previous studies have successfully demonstrated hydrogen production by autothermal reforming of light hydrocarbons using a mixed bed of Pt-based and Ni-based catalysts and/ or a composite Pt-Ni catalyst bed, with two catalytic functions on the support offered best performance [1]. However, it should be noted that the catalytic conversion of higher hydrocarbons may involve a greater tendency for coke formation. As a result, attention will be focused on utilising the two bed system consisted of a bed of Pt-based catalyst followed by a bed of Ni-based catalyst.

As the first part of the ultimate goal of producing hydrogen by autothermal reforming of gasoline-like hydrocarbons, the following objectives are set

1. To investigate the light off temperatures of higher hydrocarbons over a commercial Ni-based (Ni-com) catalyst as a benchmark, a Pt/CeO₂ catalyst as a candidate for promoting oxidation reactions, and a Pt/Ni-com catalyst as a representative of composite functions.
2. To study the influence of oxygen : carbon (O:C) ratios of the feedstock on the oxidation of higher hydrocarbons.

6.2 Experimental methods

Testing of the catalytic partial oxidation (POX) of gasoline-like hydrocarbons was undertaken using a stainless steel tubular fixed bed reactor as described in Chapter 3.

A Pt/CeO₂ (ca. 2 – 3 %wt of Pt) and a Pt/Ni-com catalyst of similar Pt loading were prepared in the laboratory using the techniques described in Chapter 4. A Ni-com naphtha

steam reforming catalyst was used as a benchmark. All catalysts were employed to observe the light off temperatures for gasoline-like hydrocarbons. Details of loading of catalysts were explained in Chapter 3. All catalysts used were unreduced.

6.2.1 Blank test

Blank runs were carried out using $\alpha\text{-Al}_2\text{O}_3$ only as a catalyst diluent under the same conditions as those employed in the partial oxidation experiments of gasoline-like hydrocarbons. The results showed that, under the conditions used, the tubing, the pre-heater, the reactor wall, and $\alpha\text{-Al}_2\text{O}_3$ diluent exhibited no reaction activities.

6.2.2 Measurement of light off temperatures (LOTs)

There is more than one definition of light off temperature (LOT). For instance, Schmidt [13] defines LOT as a certain temperature where the catalyst ignites. Ma quotes LOT as the temperature at which 10 % of fuel is converted [1]. Patterson et al. [5, 6] introduces T_{50} , a temperature required for 50 % conversion of hydrocarbons. However, in the context of autothermal reforming, it is not intended to convert all of the hydrocarbons feed into carbon dioxide and water, since at least ca. 50% of the residual fuel will be steam reformed to produce hydrogen. From preliminary experiments for the oxidation of isooctane, it was found that observing 10 % conversion was not easy. It is therefore reasonable to define TO_{50} , the temperature at which 50 % of the supplied oxygen was consumed.

The TO_{50} for the oxidation of gasoline-like fuels over Ni-com, Pt/CeO₂, and Pt/Ni-com were determined individually. The mixture of hydrocarbons or artificial gasoline was then tested over the catalyst which gave the lowest TO_{50} . Reactants (fuel, oxygen, and nitrogen) were admitted to the reactor at room temperature. The disappearance of reactants and the appearance of products were examined as a function of temperature, using a steady state control sequence. Temperature was ramped at 5°C min⁻¹ from ambient temperature and then held steady at a certain interval (ca. 25 or 50 °C) until the system stabilised. Measurements were then taken and temperatures were ramped for another set of experiment. The temperature range for all experiments was between ambient and 350 °C unless otherwise stated. Light off temperatures were examined over a range of oxygen to carbon atom ratios while gas hourly space velocity (GHSV) were kept constant unless otherwise stated.

Note that the reproducibility of the reported values of TO_{50} were within ± 5 °C.

6.3.1 Oxidation of artificial gasoline over a Ni-com catalyst

Nickel has been known as the active metal for the steam reforming of natural gas, as well as naphtha [7-12, 14-39]. In addition, hydrocarbon oxidation over nickel catalysts has also been reported [1, 40] despite the fact that platinum is known as a better catalyst for the oxidation of hydrocarbons. In the proposed autothermal hydrogen production studies, the oxidation and steam reforming of hydrocarbons are coupled. As a result, it is necessary to quantify contributions of all catalysts involved in both reactions.

Preliminary experiments involved total oxidation of cyclohexane, hexene, and isooctane as representatives of cycloalkanes, olefins, and branched alkanes over an unreduced Ni-com catalyst as a function of furnace temperature. Results are summarised in Figure 6.1.

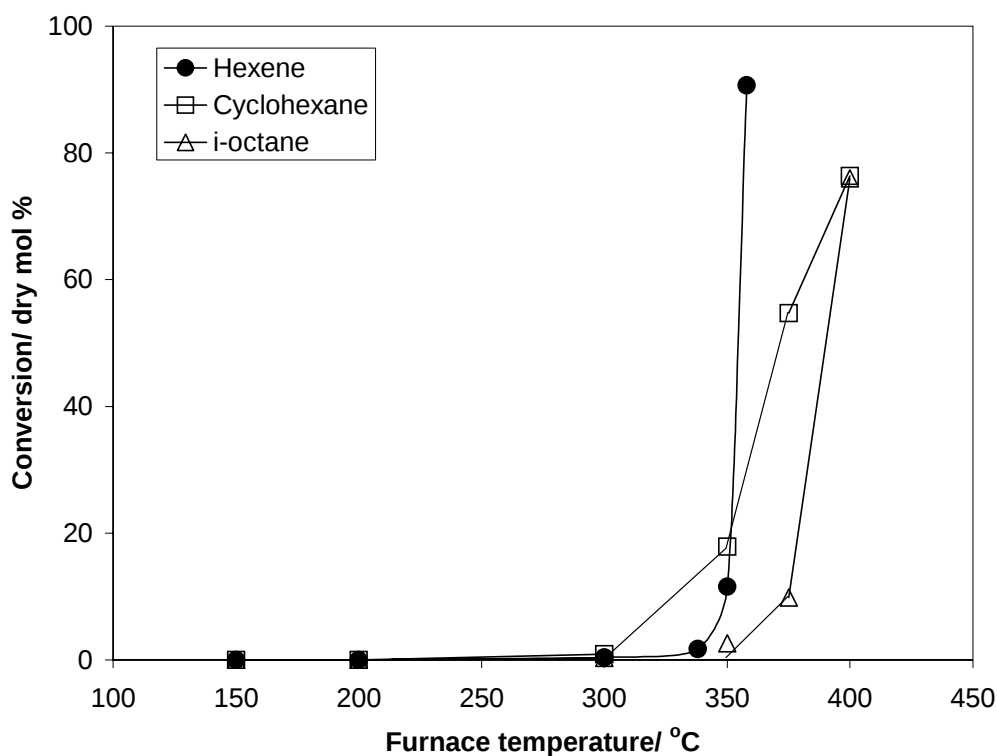


Figure 6.1. Oxidation of gasoline-like hydrocarbons over a Ni-com catalyst (O:C ca. 6 ; GHSV 65,000 h⁻¹ ; O₂ 34.3 % for hexene/19.6 % for cyclohexane/ 27.2 % for isooctane).

The unreduced Ni-com catalyst promoted oxidation of gasoline-like hydrocarbons and the light off temperatures were observed to be ca. 350 °C for hexene and cyclohexane, and ca. 375 °C for isooctane. The oxidation of hydrocarbons at low temperatures (ca. below 350 °C) was very slow. However, the catalyst bed temperature rose rapidly and the conversion increased dramatically until the limiting reactant was totally consumed, when the light off temperatures were attained.

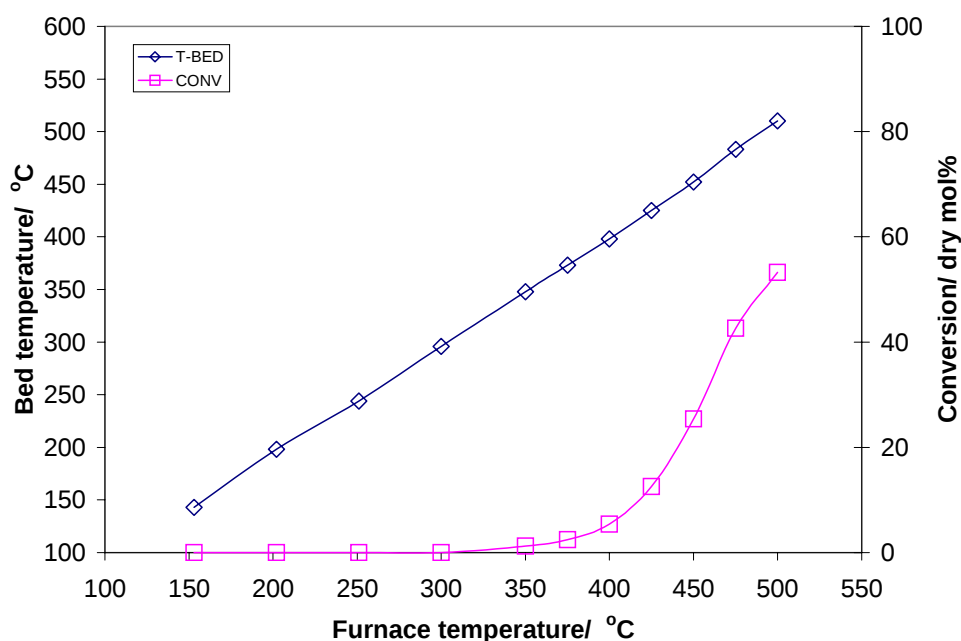


Figure 6.2. Partial oxidation of cyclohexane over a Ni-com catalyst (O:C ca. 1.5; GHSV 65,000 h⁻¹ ; O₂ 4.8 %).

Ma [1] and Hiam [41] have reported that the reactivity of saturated hydrocarbons increased (i.e. LOT decreased) as the number of carbon atoms increased. More recently, Patterson et al. [5, 6] reported the order of the reactivity for the separate reactions of benzene > toluene > hexene over Pt/alumina washcoated cordierite: however reversals in the order of oxidation for the four hydrocarbons (i.e. hexene > toluene > benzene > isooctane) were observed when they were mixed. Moro-oka et al. [42] reported the general sequence of activity decreasing from linear hydrocarbons to olefins to acetylene and to branched hydrocarbons, again over Pt. This was in agreement with the presently observed order, where isooctane was the least reactive hydrocarbon. However, it is expected that the oxygen : carbon (O:C) ratios play an important role in influencing the light off temperatures of hydrocarbons. Generally speaking, the more oxygen fed into the reactor, the lower the

light off temperatures. Figure 6.2 shows the conversion profile for cyclohexane as a function of furnace temperature at O:C ~ 1.5. It was clearly seen that the light off temperatures of oxygen limited oxidation was higher by ca. 100 °C, than its respective total oxidation value depicted by Figure 6.1 (O:C = 6:1).

From the above preliminary results, no more experiments were attempted for other gasoline-like hydrocarbons, since all of light off temperatures over Ni-com catalysts were considered too high (ca. above 300 °C) for the proposed studies of autothermal reforming.

6.3.2 Partial oxidation of artificial gasoline over a Pt/Ni-com catalyst

6.3.2.1 Light off temperatures comparison of individual hydrocarbons

Since the TO₅₀ values over Ni-com were too high, a Pt-doped Ni-com catalyst was tested in an attempt to lower the light off temperatures of gasoline-like hydrocarbons. The partial oxidation of cyclohexane, isooctane, n-octane, and toluene were individually carried out at O:C ratios of ca. 1.0 and GHSV of ca. 65,000 h⁻¹. The results are presented in Figure 6.3.

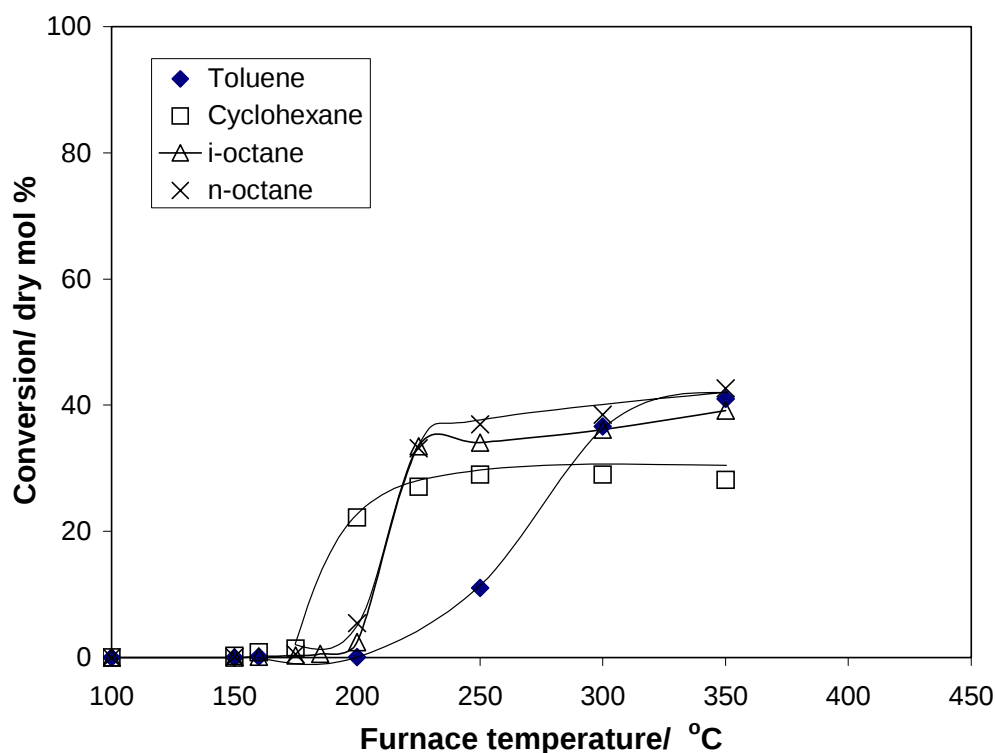


Figure 6.3 Partial oxidation of gasoline-like hydrocarbons over a Pt/Ni-com catalyst (O:C ca. 1; GHSV : 65,000 h⁻¹ ; O₂ 3.9 % for toluene/3.3% for cyclohexane/4 % for isooctane/4.8% for n-octane).

As expected, the partial oxidation of these hydrocarbons proceeded slowly at temperatures below 175 °C, but, once the hydrocarbons lit off, catalyst bed temperatures rose very rapidly and the conversion increased dramatically until oxygen was totally consumed. Extended temperature ramping to 350°C exhibited no significant conversion of hydrocarbons. This confirmed that the partial oxidation was an oxygen limited reaction. The reactivities followed the order of cyclohexane > isooctane ~ n-octane > toluene. It was clear that unsaturates were more easily oxidised in comparison to saturates viz. iso and n-octane over Pt/Ni-com catalyst.

6.3.2.2 The effect of oxygen to carbon ratios on the light off temperatures of isooctane

A series of experiments with isooctane as a model for gasoline at various O:C ratios were conducted, in order to study the relationship between feed compositions and the light off temperatures. Oxygen to carbon ratios were varied up to 0.5, 1.0, and 1.5 as a matter of a heuristic approach. The experimental sequence involved O:C of 1, 1.5, and finally 0.5 in order to maintain an experimental randomness, and to avoid a systematic experimental error due to catalyst deactivation.

Figure 6.4 depicts the dependence of isooctane conversion as a function of furnace temperature. For simplicity, only maximum temperatures of catalyst bed when the light off temperatures were attained ($T_{\max}$), were recorded on top of each conversion profile. It is seen that, as the O:C ratios increase, the light off temperatures decreases. At lower temperatures, the kinetics of oxidation dictate the rate and, as the O:C ratio increases, the rate accelerates. This generates more heat and leads to light off at lower temperatures. Once light off occurs, the rate is dictated by mass transfer effects and no major differences in behaviour are observed. However, TO_{50} for the O:C ratio of 0.5 is comparable to TO_{50} for an O:C ratio of 1.0, which could be due to the enhancement effect of catalyst reduction by hydrogen produced from previous run (O:C ratio = 1.5:1). This was supported by the evidence of catalyst reduction at relatively low temperatures as shown by TPR runs (Chapter 4). As seen in Table 6.1, the isooctane oxidation was initiated in the temperature range of 190 – 210 °C depending on the O:C ratios.

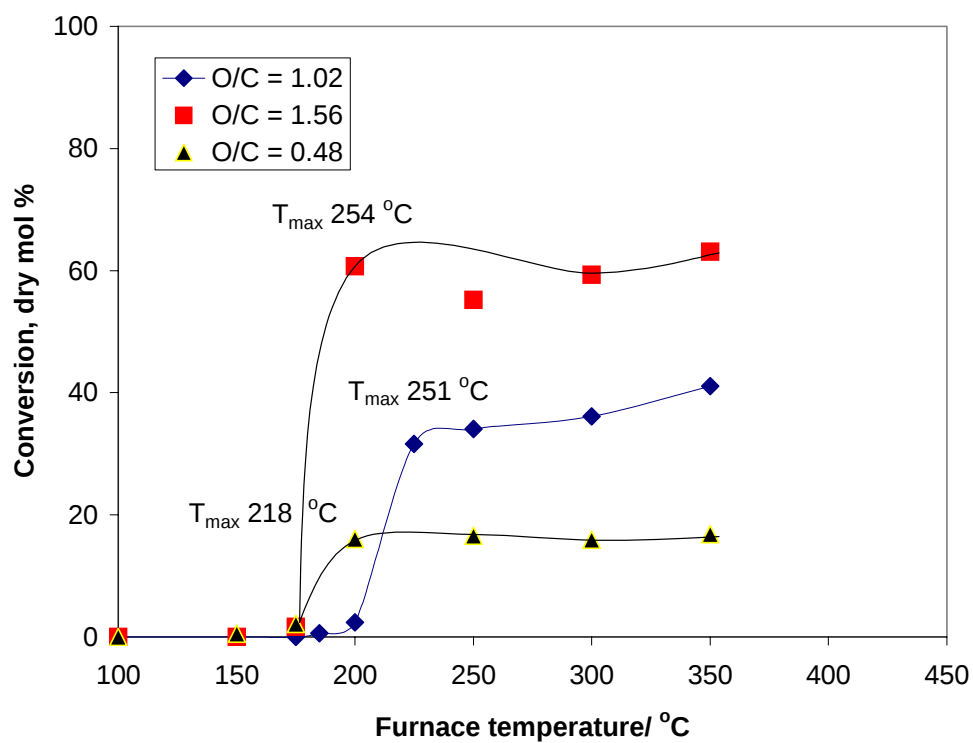


Figure 6.4 Effect of the O:C ratios on the light off temperatures for the partial oxidation of isooctane over a Pt/Ni-com catalyst (GHSV = 65,000 h⁻¹ ; O₂ 1.85 % / 4 % / 5.7 %)

Table 6.1 The light off temperatures (TO₅₀) needed, the maximum temperatures (T_{max}) and the maximum conversions achieved at various O:C ratios for isooctane over a Pt/Ni-com catalyst

R	TO ₅₀ , °C	T _{max} , °C	X _{max} , %
1.02	213	251	33.5
1.56	188	254	60.7
0.48	188	218	16.0

6.3.2.3 The effect of oxygen to carbon ratios on the partial oxidation product distribution of isooctane

Table 6.2 presents the product distribution of isooctane partial oxidation at various O:C ratios (R). As expected, O:C ratios of the reactants influenced the light off temperatures as well as partial oxidation (POX) product distributions. As seen in Table 6.2, when R were 0.5 and 1, about 20 – 30 % of isooctane fed was oxidised to carbon dioxide, and no carbon monoxide and hydrogen were observed. However, when R was increased to 1.5, about 60 % of isooctane was converted and small amounts of carbon monoxide, methane, and hydrogen were detected.

Table 6.2 Product distribution of isooctane partial oxidation at various O:C ratios (R) over a Pt/Ni-com catalyst

Species	Product composition at various O:C ratios (dry mol %) based on isooctane		
	R = 1.02	R = 1.56	R = 0.48
H ₂	0	0.77	0
CO ₂	2.66	4.21	1.19
O ₂	0.33	0.05	0.12
N ₂	96.82	95.03	97.94
CH ₄	0	0.03	0
CO	0	0.14	0
C ₈ H ₁₈	0.72	0.35	0.78

At various O:C ratios, one or more of the following reactions might be significant, as previously noted in Chapter 5 :





Once initiated, the exothermic oxidation reaction of (5.1) took place rapidly and produced a large amount of heat. Therefore, the catalyst bed temperature rose to a maximum temperature until the system stabilised. Product species were analysed in order to calculate the maximum conversion, X_{max} , achieved, as shown in Table 6.1. It was clearly seen that the higher the O:C ratio employed, the higher the T_{max} and X_{max} observed.

The heat and steam generated could be sufficient to drive reactions (5.3) and (5.4), leading to traces of carbon monoxide and hydrogen.

Based on the results from isooctane runs, it was decided to vary the O:C ratios for other hydrocarbons at 1 and 1.5 only, due to the fact that increasing O:C ratios would reduce the amount of available hydrocarbons for steam/dry reforming, and that lowering O:C ratios would decrease T_{max} and the heat needed to drive the reforming of unburnt hydrocarbons.

6.3.2.4 The effect of oxygen to carbon ratios on the light off temperatures of cyclohexane

Figure 6.5 shows the dependence of cyclohexane conversion as a function of furnace temperature. It was observed that, as the O:C ratios increased, the light off temperatures decreased (Section 6.3.2.2). As seen, the cyclohexane oxidation was initiated in the

temperature range of 200 – 225 °C depending on the O:C ratios. This was slightly higher than the light off temperature of isooctane.

It is interesting to note the differences introduced by the definition of LOT. TO_{10} gives equal LOT irrespective of O:C ratios (ca. 200 °C), while TO_{50} shows a clear effect as a result of varying O:C ratios.

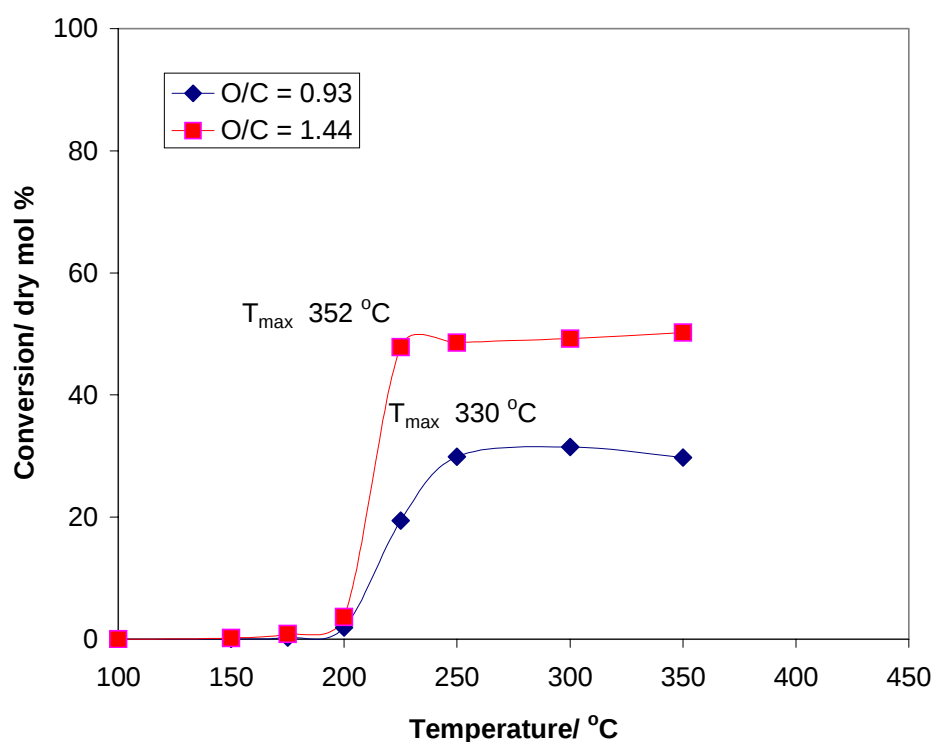


Figure 6.5 Effect of the O:C ratios on the light off temperatures for the partial oxidation of cyclohexane over a Pt/Ni-com catalyst (GHSV = 65,000 h⁻¹ ; O₂ 3.3 % and 5.2 %)

Table 6.3 summarised the light off temperatures (TO_{50}) required for initiating oxidation, the maximum temperatures reached (T_{max}) and the maximum conversions attained (X_{max}) after lighting off at various feed O:C ratios.

Table 6.3 The light off temperatures ($T_{O_{50}}$) needed, the maximum temperatures (T_{max}) and the maximum conversions achieved at various O:C ratios for cyclohexane over a Pt/Ni-com catalyst

R	$T_{O_{50}}$, °C	T_{max} , °C	X_{max} , %
0.93	225	330	29.9
1.44	213	352	47.9

As seen, X_{max} achieved was ca. 30 – 48 %, again, but slightly decreased in comparison to isooctane, despite the fact that higher T_{max} was attained. Therefore, it was not surprising that the amount of carbon monoxide and hydrogen produced (Table 6.4), was also less than from isooctane.

Table 6.4 Product distribution of cyclohexane partial oxidation at various O:C ratios (R) over a Pt/Ni-com catalyst

Species	Product composition at various O:C ratios (dry mol %) based on cyclohexane	
	R = 0.93	R = 1.44
H ₂	0	0.03
CO ₂	2.20	3.79
O ₂	0.24	0.04
N ₂	96.76	95.91
CH ₄	0	0
CO	0	0
C ₆ H ₁₂	0.86	0.69

6.3.2.5 The effect of Oxygen to Carbon ratios on the light off temperatures of n-octane

The partial oxidation of n-octane was performed, as a representation of a straight alkane contained in the gasoline. Figure 6.6 shows the light off temperature profile as a function of furnace temperatures at two O:C ratios. Again, it was observed that, as the O:C ratios increased, the light off temperatures decreased (Section 6.3.2.2). As seen, the n-octane oxidation was initiated in the

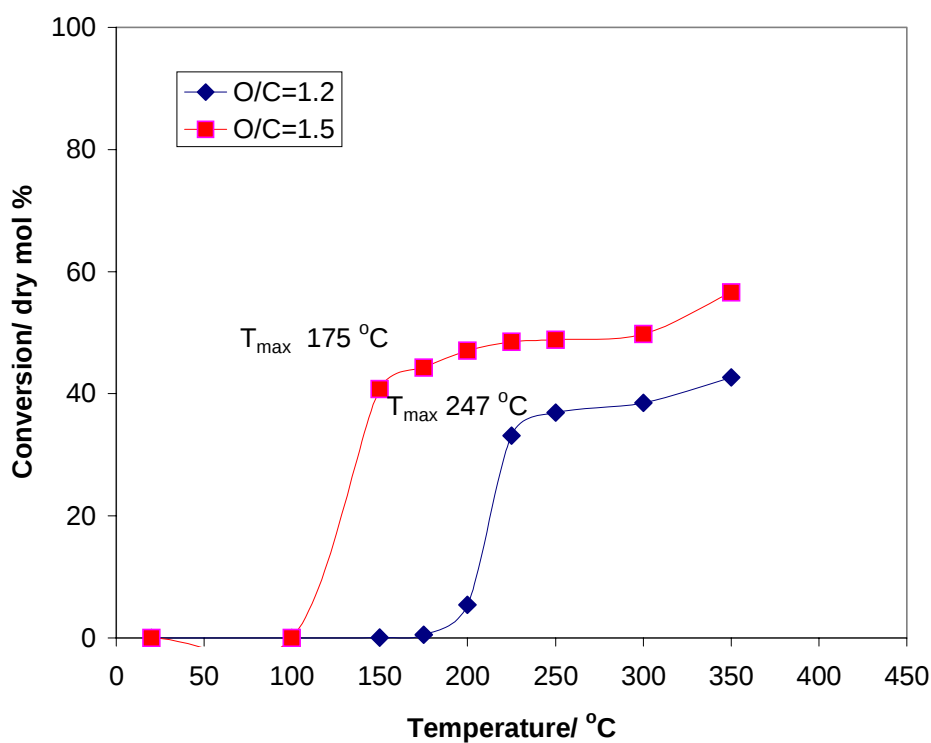


Figure 6.6 Effect of the O:C ratios on the light off temperatures for the partial oxidation of n-octane over a Pt/Ni-com catalyst (GHSV = 65,000 h⁻¹ ; O₂ 4.7 % and 5.8 %)

temperature range of 125 – 225 °C depending on the O:C ratios.

As summarised in Table 6.5, $X_{\max}$ achieved was ca. 30 – 40%, and was slightly less than from isooctane. As expected, light off temperature decreased significantly when O:C ratios were increased.

Table 6.5 The light off temperatures (TO_{50}) needed, the maximum temperatures ($T_{\max}$) and the maximum conversions achieved at various O:C ratios for n-octane over a Pt/Ni-com catalyst

R	$TO_{50}, ^\circ\text{C}$	$T_{\max}, ^\circ\text{C}$	$X_{\max}, \%$
1.2	213	247	33.2
1.5	125	175	40.7

Table 6.6 Product distribution of n-octane partial oxidation at various O:C ratios (R) over a Pt/Ni-com catalyst

Species	Product composition at various O:C ratios (dry mol %) based on n-octane	
	R = 1.2	R = 1.5
H ₂	0.00	0.00
CO ₂	3.08	3.50
O ₂	0.34	0.97
N ₂	96.13	94.89
CH ₄	0.00	0.00
CO	0.00	0.00
C ₈ H ₁₈	0.66	0.64

As shown by Table 6.6, neither hydrogen nor carbon monoxide was produced at both O:C ratios suggesting that the dominant reaction was oxidation. This was not unexpected in view of the lower $T_{\max}$ values.

6.3.2.6 The light off temperature of toluene

The partial oxidation of toluene was undertaken, as a model of an aromatic compound contained in the gasoline. The results summarised in Table 6.7 revealed that this particular compound possessed the highest light off temperature of ca. 260 °C , and the lowest $X_{\max}$ in comparison to other gasoline-like hydrocarbons. No carbon monoxide and hydrogen were produced, which indicated that toluene oxidation was dominant. Bearing in mind that toluene was the hardest compound to be oxidised, it was therefore decided not to attempt increasing the O:C ratio to 1.5.

Table 6.7 Product distribution, TO_{50} , T_{max} and X_{max} for partial oxidation of toluene (GHSV 67,000 h^{-1}) over a Pt/Ni-com catalyst

Species	Product composition (dry mol %) based on toluene
	R = 1.01
H ₂	0
CO ₂	1.89
O ₂	1.67
N ₂	95.62
CH ₄	0
CO	0
C ₇ H ₈	0.86
TO_{50} , °C	263
T_{max} , °C	307
X_{max} , %	22.2

In summary, the individual partial oxidation for artificial gasoline were undertaken over a Pt/Ni-com catalyst. The observed light off temperatures at standard testing conditions (O:C ratio of ca.1 and GHSV of ca. 65,000 h^{-1}) were found to be 213, 213, 225, and 263 °C for isooctane, n-octane, cyclohexane, and toluene respectively.

6.3.3 Partial oxidation of artificial gasoline over Pt/CeO₂ catalyst

6.3.3.1 Light off temperatures comparison of individual hydrocarbons

The partial oxidation of cyclohexane, isooctane, n-octane, and toluene were individually carried out at the same O:C ratios of ca. 1.0 and GHSV of ca. 65,000 h⁻¹. The results are presented in Figure 6.7.

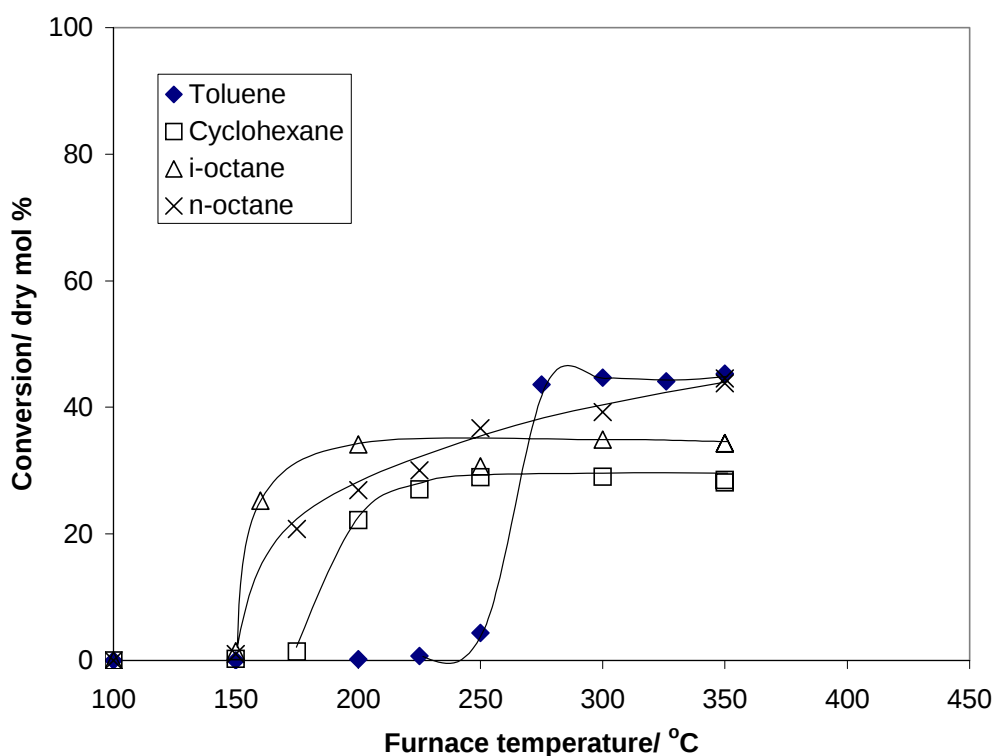


Figure 6.7 Partial oxidation of gasoline-like hydrocarbons over a Pt/CeO₂ catalyst (O:C ca.1; GHSV: 65,000 h⁻¹ ;O₂ 3.7% for toluene/3.6 % for cyclohexane/4 % for isooctane/4 % for n-octane).

As expected, the partial oxidation of these hydrocarbons proceeded slowly at temperatures of below 150 °C but, once the hydrocarbons lit off, catalyst bed temperatures rose very rapidly and the conversion increased dramatically until oxygen was totally consumed.

Extended temperature ramping to 350°C exhibited no significant conversion of hydrocarbons. This confirmed that the partial oxidation was an oxygen limited reaction. The reactivities of cyclohexane, isooctane, n-octane, and toluene followed the order of isooctane > n-octane > cyclohexane > toluene.

Again, a series of experiments with isooctane as a model for gasoline at various O:C ratios were conducted, in order to study the relationship between feed compositions and the light off temperatures. Figure 6.8 depicts the dependence of isooctane conversion as a function of furnace temperature. Space velocity was altered to 48,000 h⁻¹ by reducing the amount of nitrogen diluent in order to keep the inlet concentration of isooctane at ca. 1 % without changing the amount of catalyst loaded. Initially, GHSV of 65,000 h⁻¹ was attempted, but the observed inlet isooctane concentration was found to be 0.7 %, probably due to incorrect measurement of nitrogen diluent.

For simplicity, only maximum temperatures of the catalyst bed when the light off temperatures were attained ($T_{\max}$) are recorded on top of each conversion profile. As seen, the isooctane oxidation was initiated in the temperature range of 150 – 175 °C depending on the O:C ratios, and $T_{\max}$ increases with increasing O:C ratios.

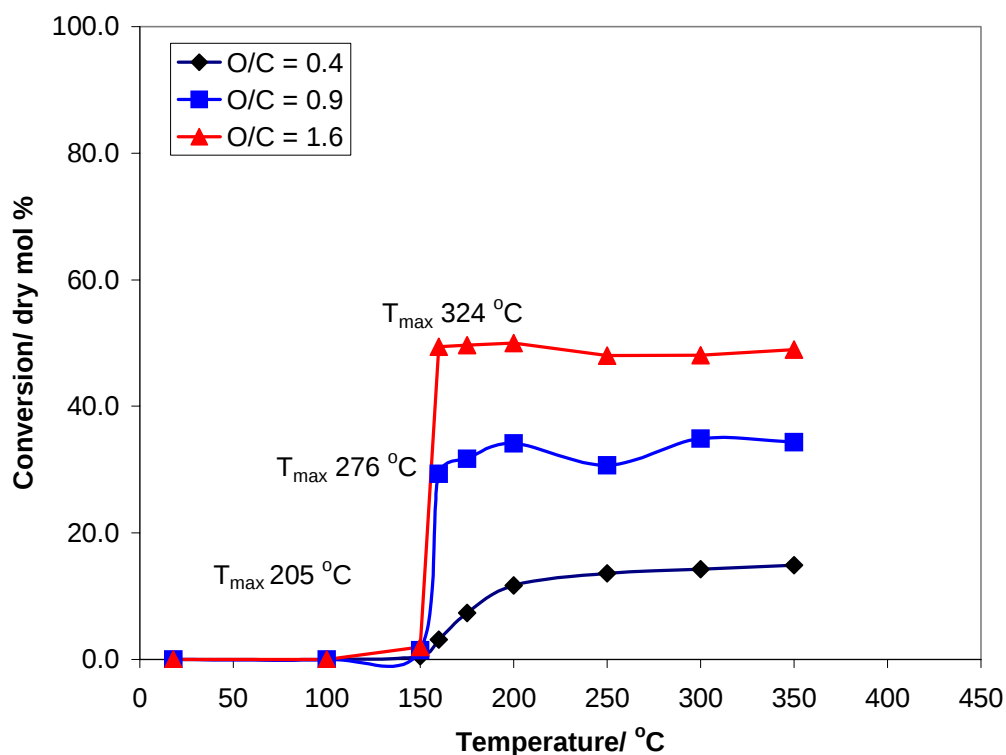


Figure 6.8 Effect of the O:C ratios on the light off temperatures for the partial oxidation of isooctane over a Pt/CeO₂ catalyst (GHSV = 48,000 h⁻¹ ;O₂ 1.9 % / 4 % / 5.7 %)

It was observed that, as the O:C ratios increased, the light off temperatures (TO₅₀) decreased (Section 6.3.2.2). However, for an O:C ratio of 0.9 gave the same TO₅₀ as an O:C ratio of 1.6. TO₁₀ remained the same.

Table 6.8 summarised the light off temperatures (TO₅₀) required for initiating oxidation, the maximum temperatures reached (T_{max}) and the maximum conversions attained (X_{max}) after lighting off at various feed O:C ratios. As seen, X_{max} achieved was ca. 7 – 49 %.

Table 6.8 The light off temperatures ($T_{O_{50}}$) needed, the maximum temperatures (T_{max}) and the maximum conversions achieved at various O:C ratios for isooctane over a Pt/CeO₂ catalyst

R	$T_{O_{50}}$, °C	T_{max} , °C	X_{max} , %
0.4	175	205	7.3
0.9	155	276	29.3
1.6	155	324	49.4

6.3.3.2 The effect of oxygen to carbon ratios on the partial oxidation product distribution of isooctane

Table 6.9 summarises the product distribution of isooctane partial oxidation at various O:C ratios (R). As expected, O:C ratios of the reactants influenced the light off temperatures as well as POX product distributions. No carbon monoxide, methane, and hydrogen were detected at all O:C ratios. This was as expected since essentially the oxidation of isooctane was predominant over Pt/CeO₂ catalyst in comparison to Pt/Ni-com catalyst, and the temperature was not high enough to favour steam reforming.

Table 6.9 Product distribution of isooctane partial oxidation at various O:C ratios (R) over a Pt/CeO₂ catalyst

Species	Product composition at various O:C ratios (dry mol %) based on isooctane		
	R = 0.4	R = 0.9	R = 1.6
H ₂	0.00	0.00	0.00
CO ₂	0.64	2.69	3.91
O ₂	0.87	0.20	0.10
N ₂	97.48	96.30	95.48
CH ₄	0.00	0.00	0.00
CO	0.00	0.00	0.00
C ₈ H ₁₈	1.01	0.81	0.50
T _{max} , °C	205	276	324

6.3.3.3 The effect of oxygen to carbon ratios on the partial oxidation product distribution of cyclohexane

Figure 6.9 shows the dependence of cyclohexane conversion as a function of furnace temperature. As before, as the O:C ratios increased, the light off temperatures decreased prior to the attainment of light off temperatures. It is apparent that, cyclohexane oxidation was initiated in the temperature range of 150 – 200 °C depending on the O:C ratios. This

was slightly higher in comparison to the light off temperature of isooctane, which could be due to the lower reactivity of cyclohexane. Table 6.10 summarised the light off temperatures (TO_{50}) required for initiating oxidation, the maximum temperatures reached (T_{max}) and the maximum conversions attained (X_{max}) after lighting off at various feed O:C ratios.

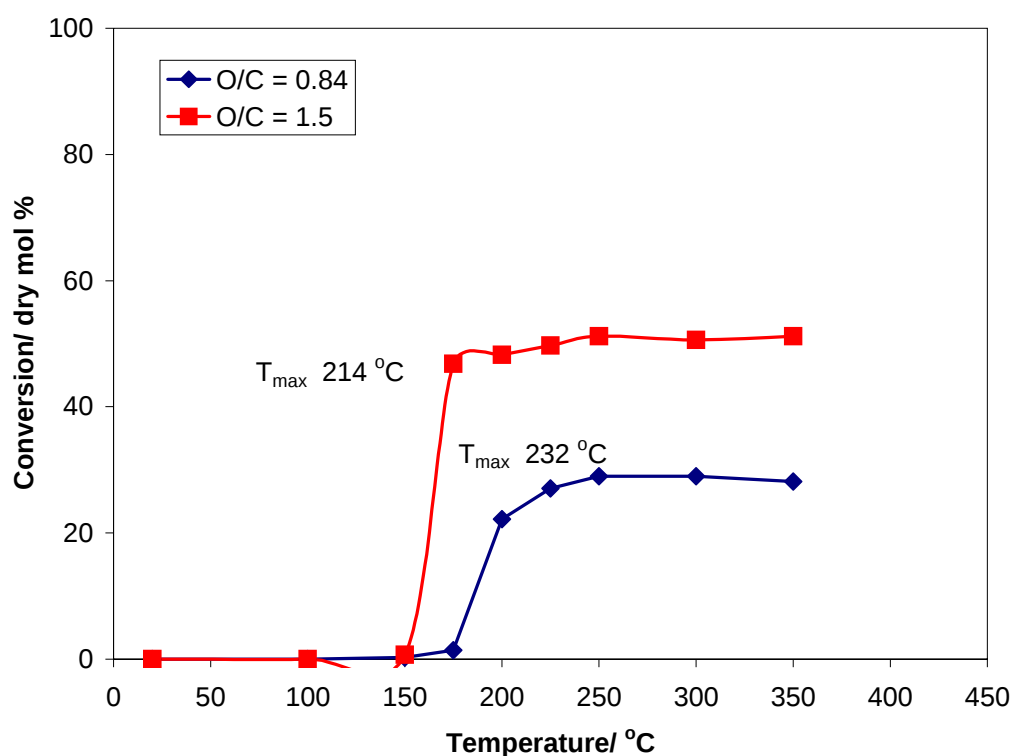


Figure 6.9 Effect of the O:C ratios on the light off temperatures for the partial oxidation of cyclohexane over a Pt/CeO₂ catalyst (GHSV = 65,000 h⁻¹ ; O₂ 3.6 % and 5.2 %)

Table 6.10 The light off temperatures (TO_{50}) needed, the maximum temperatures (T_{max}) and the maximum conversions achieved at two O:C ratios for cyclohexane over a Pt/CeO₂ catalyst

R	TO_{50} , °C	T_{max} , °C	X_{max} , %
0.84	188	232	22.2
1.5	163	214	46.8

Table 6.11 Product distribution of cyclohexane partial oxidation at various O:C ratios (R) over a Pt/CeO₂ catalyst

Species	Product composition at various O:C ratios (dry mol %) based on cyclohexane	
	R = 0.84	R = 1.5
H ₂	0.00	0.00
CO ₂	1.90	3.62
O ₂	0.86	0.18
N ₂	96.13	95.51
CH ₄	0.00	0.00
CO	0.00	0.00
C ₆ H ₁₂	1.11	0.69

6.3.3.4 The effect of oxygen to carbon ratios on the partial oxidation of n-octane

Figure 6.10 shows the light off temperature profile as a function of furnace temperatures at two O:C ratios. Again, it was observed that, as the O:C ratios increased, the light off temperatures decreased (Section 6.3.2.2). As seen, the n-octane oxidation was initiated in the temperature range of 150 – 175 °C depending on the O:C ratios. This is consistent with

the finding for cyclohexane and isooctane oxidation. It seems that the higher TO_{50} has to do with the C-H bond strength in these hydrocarbons. C-H in cyclohexane has probably higher bond strength than both isooctane and n-octane [43].

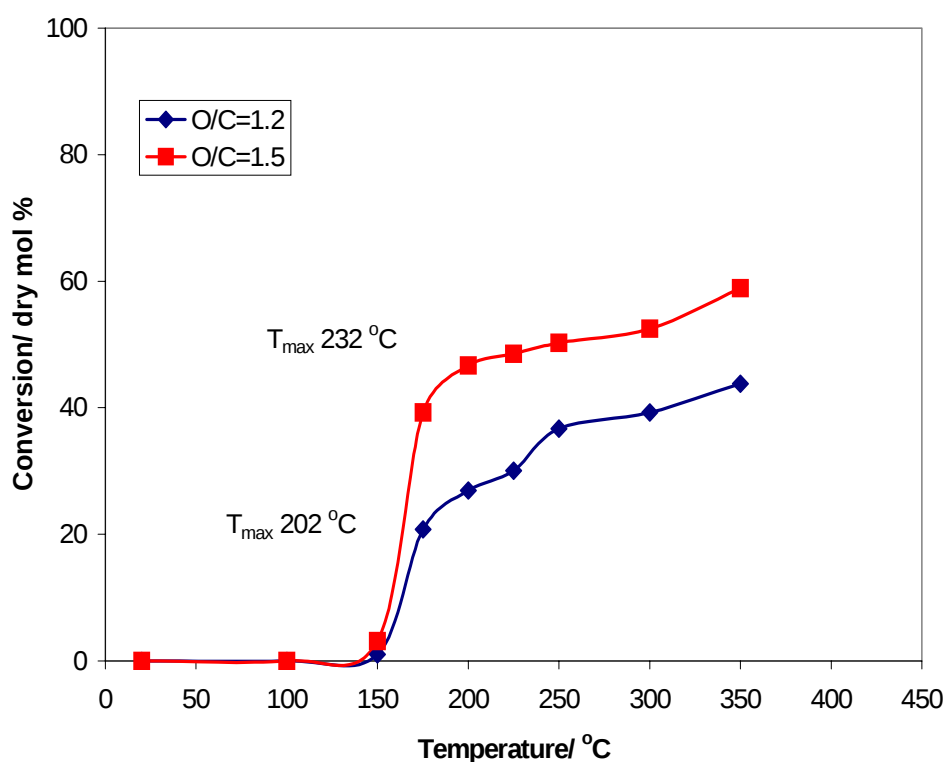


Figure 6.10 Effect of the O:C ratios on the light off temperatures for the partial oxidation of n-octane over a Pt/CeO₂ catalyst (GHSV = 65,000 h⁻¹ ; O₂ 4.6 % and 5.8 %)

As summarised in Table 6.12, X_{max} achieved was ca. 20 – 40%, and was slightly less than with isooctane. However, no differences in light off temperature were observed when O:C ratio was increased.

Table 6.12 The light off temperatures (TO_{50}) needed, the maximum temperatures (T_{max}) and the maximum conversions achieved at two O:C ratios for n-octane over a Pt/CeO₂ catalyst

R	$TO_{50}, ^\circ C$	$T_{max}, ^\circ C$	$X_{max}, \%$
1.2	163	202	20.8
1.5	163	232	39.2

Table 6.13 Product distribution of n-octane partial oxidation at various O:C ratios (R) over a Pt/CeO₂ catalyst

Species	Product composition at various O:C ratios (dry mol %) based on n-octane	
	R = 1.2	R = 1.5
H ₂	0.00	0.00
CO ₂	1.57	3.39
O ₂	2.26	1.02
N ₂	95.43	94.93
CH ₄	0.00	0.00
CO	0.00	0.00
C ₈ H ₁₈	0.75	0.66

6.3.3.5 The light off temperatures of toluene

The partial oxidation of toluene was also undertaken over Pt/CeO₂ catalyst at a standard condition, and results were summarised in Table 6.14. As seen, this particular compound possessed the highest light off temperature of ca. 260 °C , and the highest T_{max} was observed. As a result, the highest X_{max} was attained in comparison to other gasoline-like hydrocarbons.

Table 6.14 Product distribution, TO₅₀, T_{max} and X_{max} for partial oxidation of toluene (O:C = 1; GHSV 65,000 h⁻¹) over a Pt/CeO₂ catalyst

Species	Product composition (dry mol %) based on toluene
	R = 1.0
H ₂	0.03
CO ₂	3.13
O ₂	0.06
N ₂	96.21
CH ₄	0.00
CO	0.00
C ₇ H ₈	0.58
TO ₅₀ , °C	263
T _{max} , °C	364
X _{max} , %	43.6

In summary, the individual partial oxidation for gasoline-like hydrocarbons were undertaken over a Pt/CeO₂ catalyst. The observed light off temperatures at standard testing conditions (O/C ratio of ca.1 and GHSV of ca. 65,000 h⁻¹) were found to be 155, 163, 188, and 263 °C for isooctane, n-octane, cyclohexane, and toluene respectively.

6.3.4 Activity comparison of Pt/CeO₂ and Pt/Ni-com for the oxidation of artificial gasoline

Figure 6.11 shows a comparison between platinum based catalyst deposited onto two different supports. Using a commercial nickel catalyst as a support, it was clearly seen that the light off temperatures of all hydrocarbons tested were observed between 200 – 225 °C except that for toluene which was ca. 263 °C. It was evident that the use of ceria as a support remarkably lowered the light off temperatures of hydrocarbons. However, this was not the case for toluene.

This is not unexpected since the inductive effect of methyl groups on aromatic rings enhances the electron donor behaviour of the molecule and strengthens their adsorption on metallic sites: this leads to inhibition of the oxidation of the aromatic molecule [44, 45].

In conclusion, from the individual tests of hydrocarbons, ceria supported platinum catalyst was observed as the best catalyst for the oxidation of gasoline-like fuels. As a result, the partial oxidation of artificial gasoline (mixture of gasoline-like hydrocarbons) over Pt/CeO₂ was studied in more detail and the results are reported in the following section.

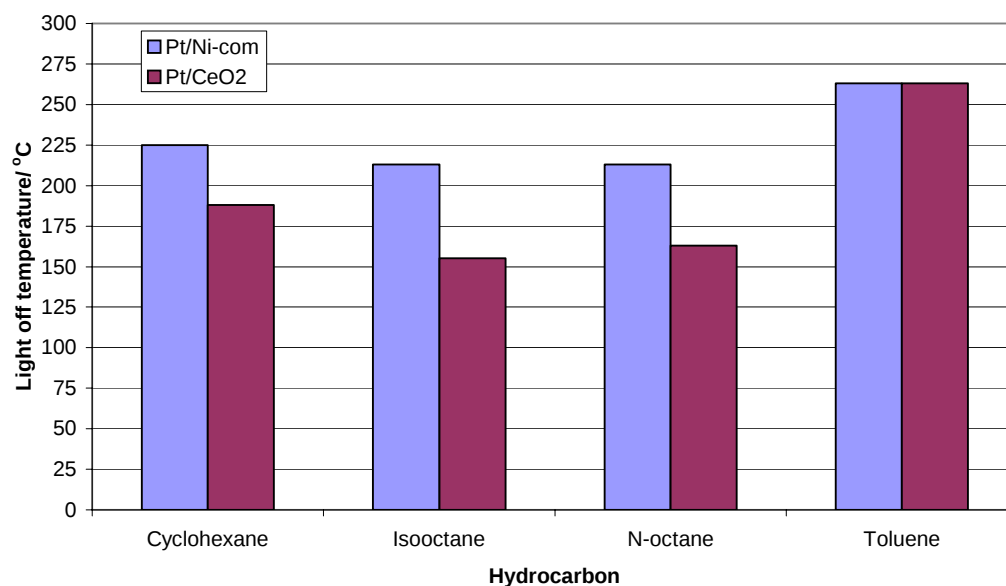


Figure 6.11. Light off temperature comparison for the partial oxidation of gasoline-like hydrocarbons over Pt/Ni-com and Pt/CeO₂ catalysts (O:C ratio~ 1; GHSV ~ 65,000 h⁻¹)

6.3.5 Activity comparison of Pt/CeO₂ for the partial oxidation of various artificial gasoline

Similar experiments for the partial oxidation of the three different formulation of artificial gasoline were undertaken over Pt/CeO₂ under the same standard conditions employed in Section 6.3.4. Table 6.15 summarises artificial gasoline compositions being used.

Table 6.15 Artificial gasoline compositions

Compound (v/v %)	Cyclohexane	1-Hexene	Isooctane	Octane	Toluene
Mix#1	-	5	35	20	40
Mix#2	5	-	35	20	40
Mix#3	-	-	58.4	33.3	8.3
Control	-	-	100	-	-

The first mixture (denoted as Mix#1) involved 1-hexene, isooctane, normal octane, and toluene under the liquid phase composition of 5, 35, 20, and 40 v/v % respectively. Results are shown in Figure 6.12. Hexene was found to react faster than toluene and n-octane, while isooctane was the slowest reactant. No hexene alone was tested separately over this particular catalyst, but, oxidation over a Ni-com catalyst revealed a similar behaviour (Figure 6.2). Thus, it appears that hexene adsorbs in preference to toluene, and toluene in preference to n-octane, and n-octane in preference to isooctane. It seems that surface coverage rather than intrinsic reactivity determines the order of removal in the mixture [5, 6].

The order of adsorption strength of hexene > toluene > n-octane is expected due to the adsorption of unsaturated hydrocarbons involving donation of π electrons to the vacant d orbitals of the metal. The more delocalised the π electrons, the weaker the adsorbate/metal interaction, leading to weaker adsorption of toluene compared to hexene [5].

The order of adsorption strength of n-octane > i-octane is also not surprising since theoretically straight alkanes are easier to be oxidised than branched alkanes [46, 47].

The second mixture (denoted as Mix#2) involved similar composition of Mix#1 except that 5 % hexene was replaced by 5 % cyclohexane. Results are shown in Figure 6.13 and 6.14. It is seen that toluene reacts faster than n-octane, while i-octane is the slowest reactant but only slightly behind cyclohexane. Thus, it appears that toluene adsorbs in preference to n-octane, and n-octane in preference to cyclohexane, and cyclohexane in preference to isooctane. Increasing the O:C ratios from 1 to 1.5 increases the rate and TO_{50} was found to decrease by ca. 25 °C. Thus, the reaction must be positive order in oxygen

(Figure 6.14). The slightly increasing conversion at 150 °C was probably due to the incidental variation of hydrocarbons feed composition.

Mix#3 was designed to be unsaturate and cyclic hydrocarbon free, but the ratio of isooctane : toluene : n-octane is kept the same as Mix#1 and Mix#2. The light off results are shown in Figure 6.15. Toluene is oxidised faster than other components and consistently, isooctane is always the slowest reactant which is similar to Mix#1 and Mix#2.

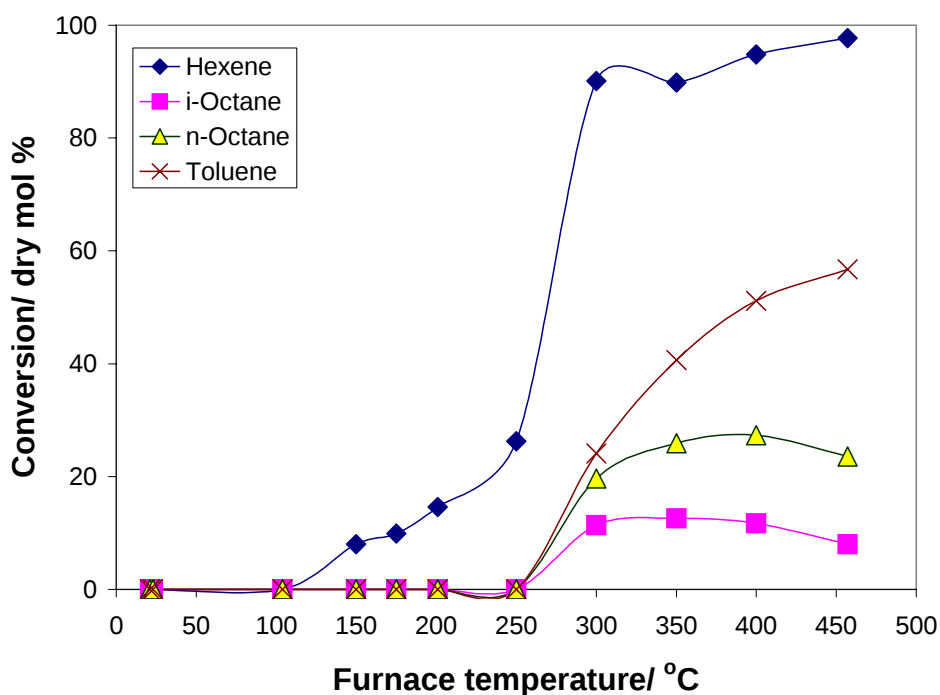


Figure 6.12 Conversion profile for the partial oxidation of Mix#1 over a Pt/CeO₂ catalyst (GHSV ~ 65,000 h⁻¹; O:C ~ 1; O₂ 3.9 %; 0.12 g unreduced catalyst; total flow 284 mL min⁻¹)

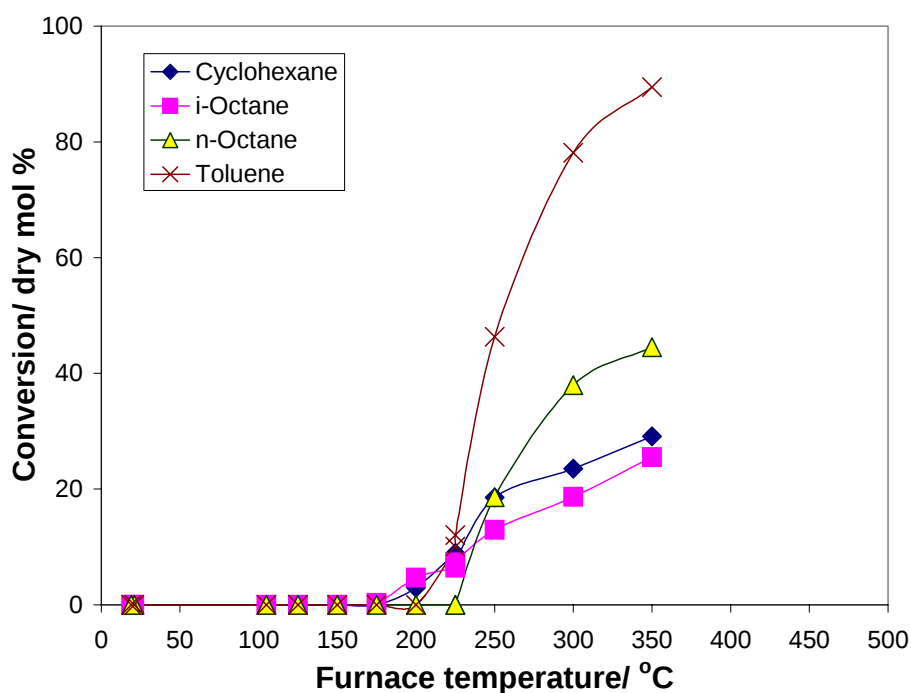


Figure 6.13 Conversion profile for the partial oxidation of Mix#2 over a Pt/CeO₂ catalyst (GHSV~65,000 h⁻¹; O:C ~ 1; O₂ 3.8 %; 0.12 g unreduced catalyst; total flow 283 mL min⁻¹)

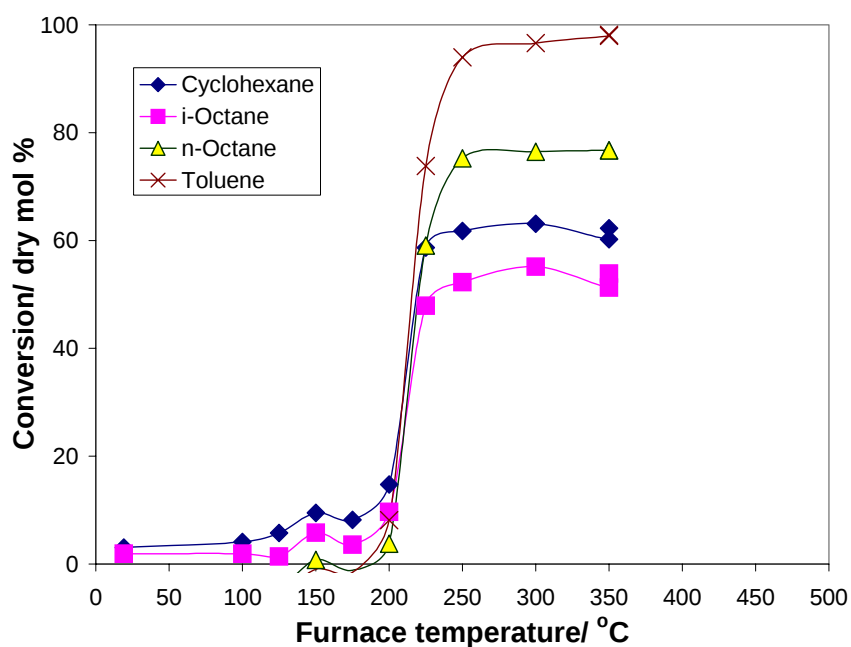


Figure 6.14 Conversion profile for the partial oxidation of Mix#2 over a Pt/CeO₂ catalyst (GHSV~65,000 h⁻¹; O:C ~ 1.5; O₂ 5.9 %; 0.12 g unreduced catalyst; total flow 285 mL min⁻¹)

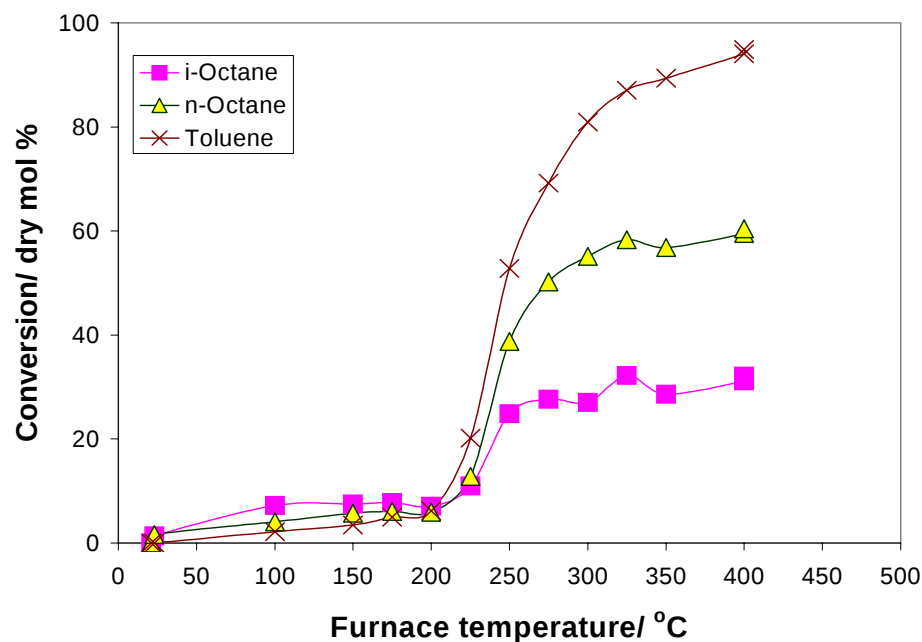


Figure 6.15 Conversion profile for the partial oxidation of Mix#3 over a Pt/CeO₂ catalyst (GHSV~65,000 h⁻¹; O:C ~1.0; O₂ 3.9 %; 0.12 g unreduced catalyst; total flow 286 mL min⁻¹)

The results for the partial oxidation of three mixtures of artificial gasoline clearly exhibits that isooctane is always the slowest reactant. In other words, isooctane oxidation does not commence until all the other components have been oxidised. This is not unexpected and may be rationalised based on the concept of relative adsorption strength [41, 42, 44, 45, 48]. Stronger hydrocarbon adsorption such as hexene and toluene will cover metal active sites. As a result, the amount of oxygen coverage will be reduced for the oxidation of other hydrocarbons. (p.184)

Examination of Figure 6.13 and 6.15 reveals that toluene exhibits higher adsorption strength relative to n-octane, cyclohexane and isooctane. Thus, not much oxygen is available to oxidise other hydrocarbons after toluene had been oxidised. Apparently,

cyclohexane does not have too much effect on the order of activity of toluene > n-octane > isooctane.

Similarly, hexene is found to have a higher adsorption strength relative to toluene, n-octane and isooctane as depicted by Figure 6.12. Accordingly, not much oxygen is left to oxidise other hydrocarbons after hexene consumed it. The activity order of hexene > toluene > n-octane > isooctane is consistent with conversion profile shown by Figure 6.15.

Apparently, n-octane is relatively easier to oxidise than isooctane. This is as expected since oxidation of alkanes requires the abstraction of a hydrogen atom, which is favoured by longer distances between C-H bond to be broken and methyl groups [44, 46].

6.4 *The comparison between Rh/CeO₂-ZrO₂ and Pt/NiO-based catalysts for the partial oxidation of isooctane*

Studies of the rhodium based catalysts for the partial oxidation of isooctane have been carried out and reported in Chapter 5, whilst similar studies over Pt/NiO based system are reported in this chapter. Table 6.16 is intended to compare results to check if there is a significant advantage in using rhodium over Pt/NiO based catalysts.

Table 6.16 The conversion and H₂ produced for the partial oxidation of isooctane over Rh and Pt/NiO based catalysts

Catalyst	Conversion, %	H ₂ produced, % v/v	Remarks
Rh/CeO ₂ -ZrO ₂	50	0.0	From Fig. 5.10 and Fig. 5.21
Pt/NiO	61	0.8	From Table 6.1 and Table 6.2

(O:C ratio = 1.56 :1; temperature range 190~250 °C)

Rhodium is seen to offer no particular advantage over the Pt and Ni based catalyst combination. As a result, no further studies were focused on the metal.

6.5 Activity comparison of Pt/CeO₂ for the partial oxidation of individual hydrocarbons with the same hydrocarbon in a mixture

It was found that ceria supported catalyst was observed as the best catalyst for the oxidation of higher hydrocarbons (Section 6.3.4) and detailed studies of the partial oxidation of artificial gasoline were carried out (Section 6.3.5). It is intended to examine the behaviour of individual compound alone and in a mixture. In such a case, results for light-off temperatures (TO₅₀) over Pt/CeO₂ catalyst at standard conditions (Figure 6.13 and Figure 6.15) for different mixtures of artificial gasoline were compared with results obtained from individual hydrocarbon representing the artificial mixtures as shown by Table 6.17.

Table 6.17 Comparison of the LOT value for individual hydrocarbons with the same hydrocarbon in a mixture over Pt/CeO₂ catalyst

Hydrocarbon	Individual LOT (°C)	LOT in Mix#2 (°C)	LOT in Mix#3 (°C)
i-Octane	155	Not achieved	Not achieved
n-Octane	163	Not achieved	275
Cyclohexane	188	Not achieved	-
Toluene	263	260	250

Essentially, the LOT of toluene is almost the same either alone or in any mixture. The conversions of other hydrocarbons are less than 50 % except n-octane in Mix#3. This finding further confirms that not much oxygen is available to oxidise other species after toluene had been oxidised.

6.6 Conclusions

Figure 6.16 shows a summary of light-off temperatures (TO₅₀) based on the total conversion as a function of furnace temperature for all mixtures.

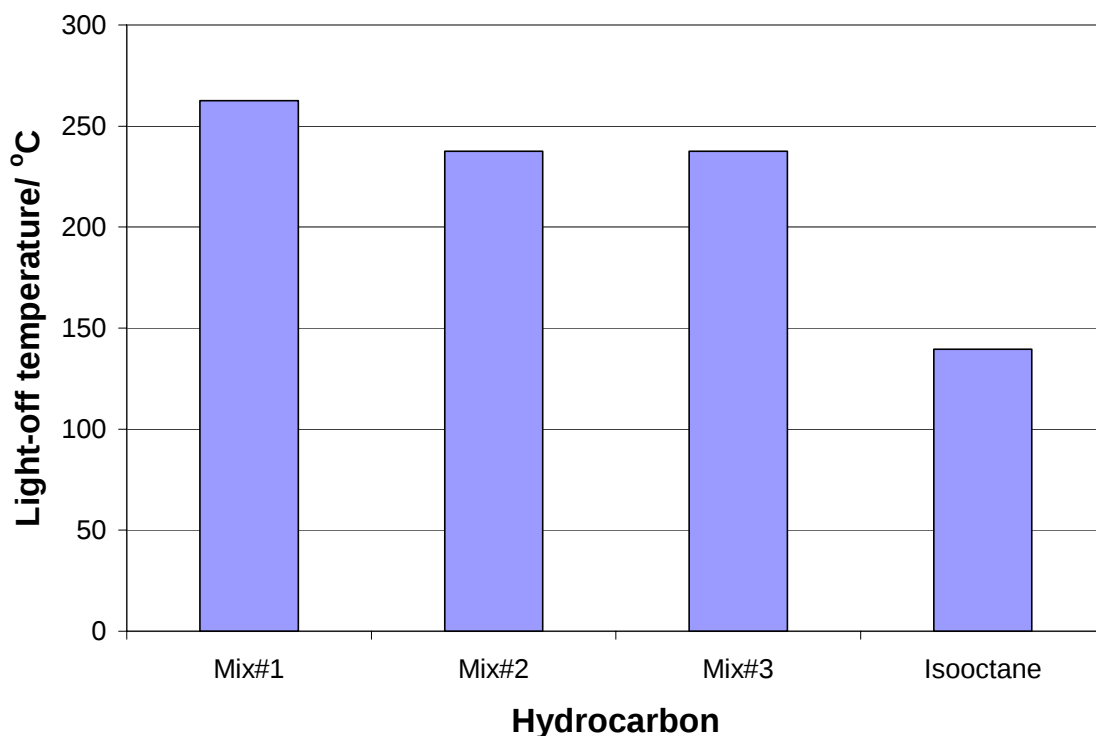


Figure 6.16 Light-off temperatures for various artificial gasoline over Pt/CeO₂ catalysts (GHSV ~ 65,000 h⁻¹; O:C = 1.0).

It is apparent that, Mix#1 exhibits the highest TO₅₀ at ca. 260 °C which is essentially the same as LOT of toluene. There is no significant difference between Mix#2 and Mix#3 which both lit off at ca. 240 °C. The light-off temperature of isooctane as a control point is reproducible at 150 ± 5 °C. In comparison to the reactivity of individual hydrocarbons which is reflected by lowering of TO₅₀, the order follows i-octane > n-octane > cyclohexane > toluene as depicted by Figure 6.11, while reversals in the order of oxidation is evident in Mix#2 (toluene > n-octane > cyclohexane > i-octane). Thus, it confirms that stronger adsorption of aromatic viz. toluene reduces oxygen coverage over the metal surface and this leads to a lower rate on other hydrocarbons.

6.7 References

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Chapter 7 Introduction to the steam reforming of artificial gasoline

7.1 *Introduction*

The steam reforming of hydrocarbons is a mature process for the production of synthesis gas for methanol, higher alcohols, and ammonia. In refineries, hydrogen is used for desulphurisation, hydrotreating, and in the production of chemicals [1, 2]. More recently, the increasingly stringent legislation for the control of vehicle exhaust emissions has led to consideration of alternative means of reducing emissions, with fuel cell powered vehicle as one favoured possibility for the replacement of the internal combustion engine [3-5]. The optimal unit for transport application has been found to be the proton exchange membranes (PEMFC) using hydrogen as a fuel [6-10].

The production of hydrogen by steam reforming technologies is an endothermic process which requires elevated temperatures and the heat needed is supplied externally [11]. In the context of fuel cells application, more interest are focused on autothermal operation in which part of fuel is burned by limited oxygen in order to produce the heat required for driving the steam reforming reaction of the remaining fuel [12, 13].

Autothermal reforming is a complex process in which both oxidation and steam reforming are involved and promoted by more than one type of supported metal catalyst: therefore

the design is considered as an optimisation routine [14-16]. The reactivity of fuels toward oxidation, the kinetics of steam reforming, the transport of heat and mass in the system, and the manipulation of operating conditions are considered as basic information for the design of such a process.

Detailed studies of the oxidation of artificial gasoline have been carried out and are reported in Chapter 6. The following chapter presents the results of studies of steam reforming of gasoline-like hydrocarbons. Two objectives are set, namely to investigate the minimum temperature required for the attainment of a significant hydrocarbons conversion (light-out temperature), and to scrutinise the hydrocarbon candidates based on the severity toward coke formation in order to formulate the mixture of an artificial gasoline.

Carbon formation plays an important role in steam reforming reactions. Either quantitative or qualitative assessment of carbon deposited may give a comparable evaluation of deactivation mode and its function on partial oxidation and steam reforming reaction. Consequently, this will contribute to a better selection of an optimal artificial gasoline composition not only based on activity and selectivity but also on catalyst stability. In this study, the relative amount of carbon deposited was followed by monitoring pressure drop built-up across the catalyst bed (a qualitative assessment) during catalyst stability test. No rigorous deactivation study was attempted.

7.2 Blank tests

Blank runs were carried out in a reactor charged with $\alpha\text{-Al}_2\text{O}_3$ (a catalyst diluent) only under the steam reforming conditions at a mild temperature (ca. 350 °C). There was no detectable activity due to the reactor wall and catalyst diluent.

7.3 Steam reforming of individual gasoline-like hydrocarbons

Preliminary experiments involved steam reforming of isooctane as a model for gasoline over a Ni-com catalyst. Prior to use, the catalyst was reduced in-situ in accordance to the method described in Chapter 3. A steam to carbon ratio of ca. 3 was applied in order to avoid carbon formation. Figure 7.1 shows the conversion profile of isooctane as a function of the catalyst bed temperature. As seen, the light-out temperature was between 300 – 400°C. As expected, this conversion profile was below the predicted profile based on thermodynamics (Figure 5.17.b of Chapter 5).

A twenty four hour stability test was then carried out at ca. 350°C and the results are plotted in Figure 7.2. Initial conversion was relatively high and it slightly decreased after 15 hours of operation. Stable conversion up to 24 hours was then observed.

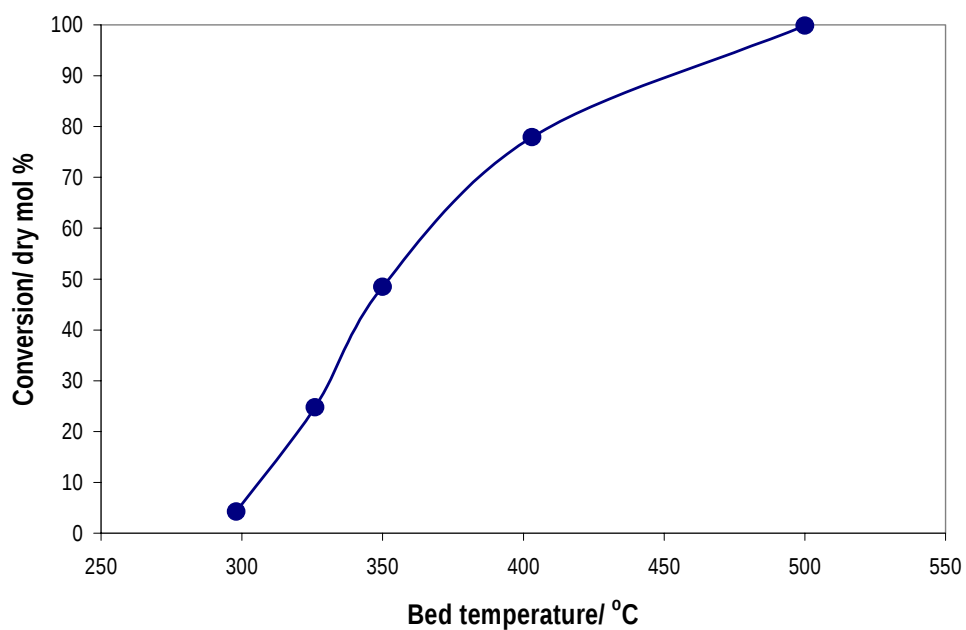


Figure 7.1 Conversion profile for the steam reforming of isooctane (GHSV 19000 h⁻¹; inlet isooctane 1.1 wet mol %; S:C 2.9; Ni-com catalyst loaded 0.44 g; Nitrogen as a diluent; Total dry flow 114 mL min⁻¹; water flow 2.0 mL h⁻¹).

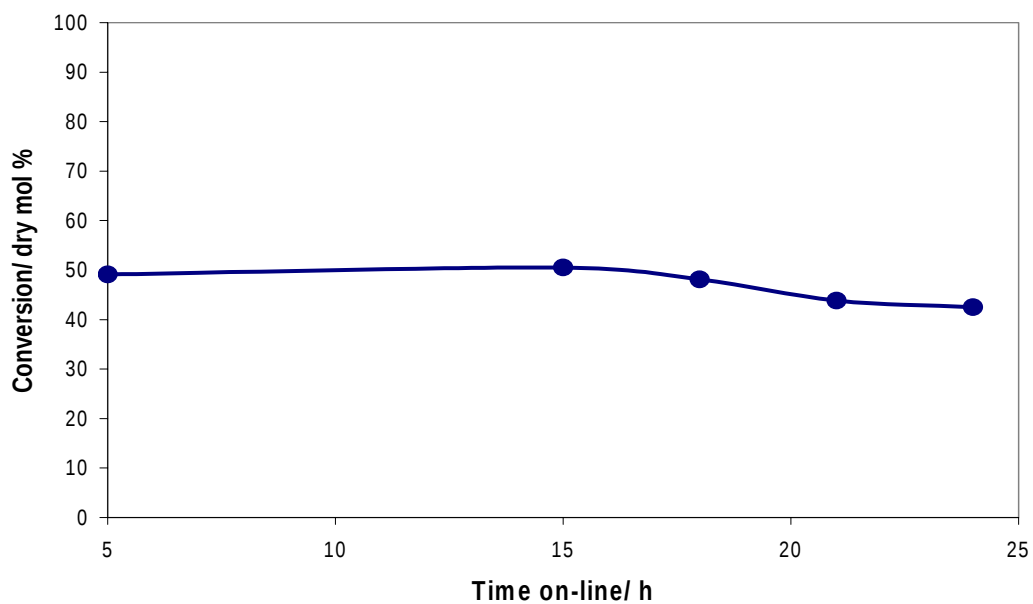


Figure 7.2 Stability test for steam reforming of isooctane at 350 °C (other operating conditions were similar to Figure 7.1)

The second hydrocarbon was cyclohexane, used as a representation of a cyclic hydrocarbon compound in gasoline. A conversion profile as a function of bed temperatures and a 24 hour stability test are displayed in Figure 7.3 and Figure 7.4 respectively.

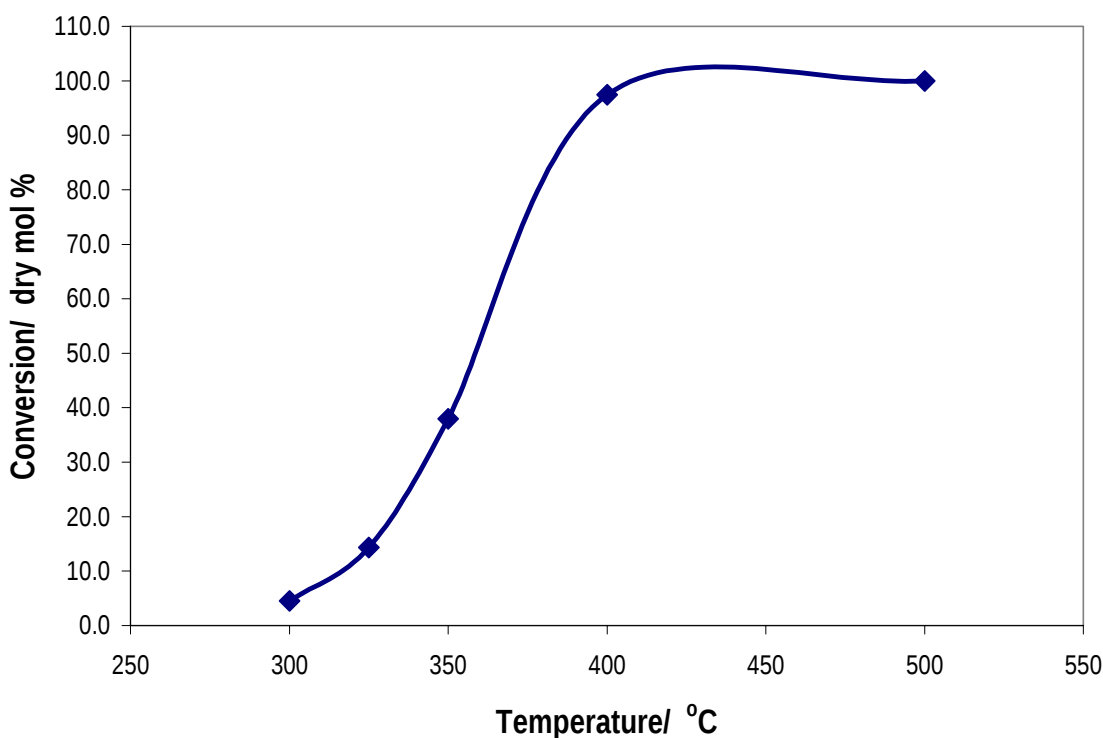


Figure 7.3 Conversion profile for the steam reforming of cyclohexane (GHSV 19000 h⁻¹; inlet cyclohexane 1.7 wet mol %; S:C 3.6; Ni-com catalyst loaded 0.50 g; Nitrogen as a diluent; Total dry flow 112 mL min⁻¹; water flow 3.1 mL h⁻¹).

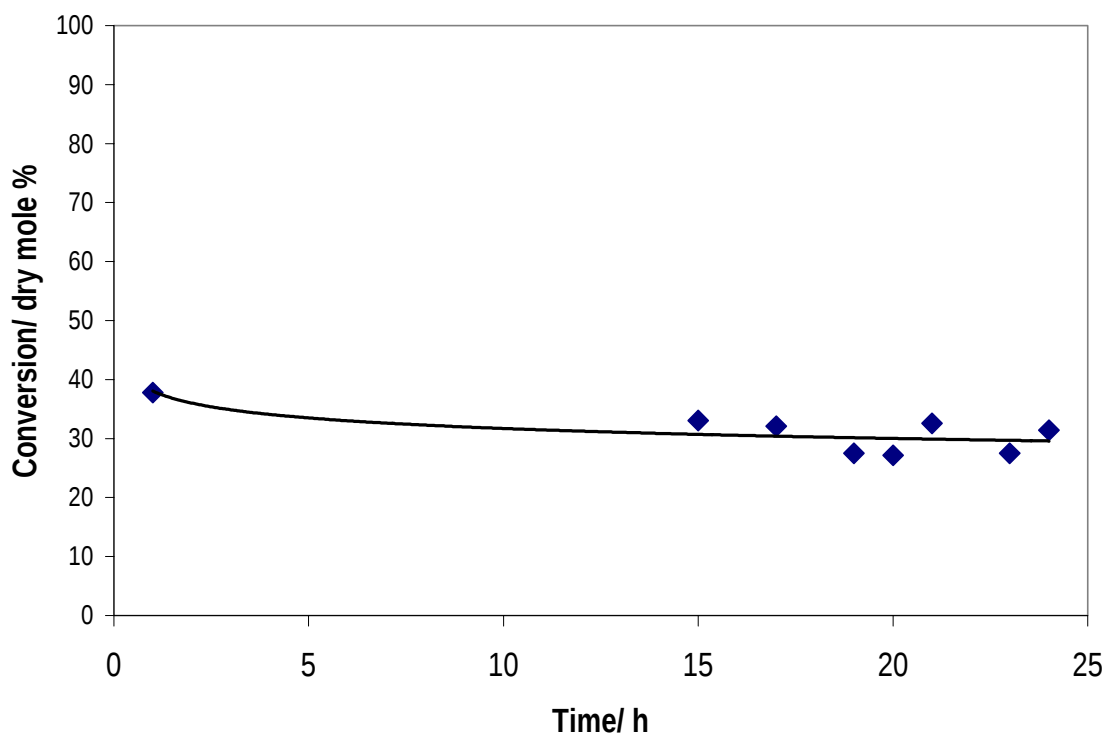


Figure 7.4 Stability test for steam reforming of cyclohexane at 350 °C (other operating conditions were similar to Figure 7.4)

As seen, the light out temperature was observed between 300 – 400 °C and the overall conversion was very stable over 24 hours of operation.

An olefin compound in gasoline was represented by 1-hexene. Steam reforming experiment at the same GHSV and a steam:carbon ratio between 2 – 3 was carried out, but the pressure drop across the catalyst bed increased rapidly (more than double the initial start up) within less than 2 hours. Data logging at a steady state condition could not be performed and the system was shut down. The catalyst was decoked at 600 °C for 4 hours under 3 % oxygen in helium and subsequently was cooled to ambient and re-reduced using similar methods to the other catalysts. An attempt was then made to run the system by doubling S:C to ca. 4.5 (therefore the GHSV was become 22500 h⁻¹). The data

logging were carried out within the first 4 hours of operation, despite the fact that the pressure drop of catalyst bed increased steadily, but at a relatively lower rate than previous run. However, when the bed temperature was increased to 500 °C, the pressure drop increased very rapidly and the system was shut down again. As a result, no stability test was undertaken. Figure 7.5 displays the observed conversion profile.

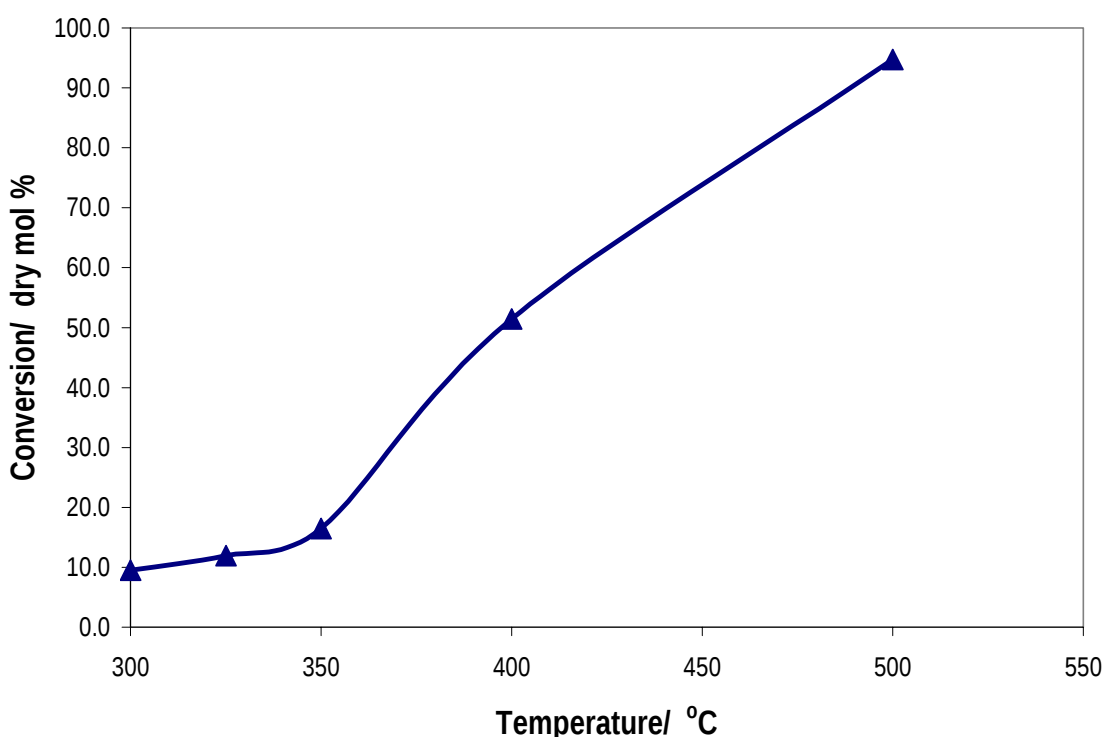


Figure 7.5 Conversion profile for the steam reforming of 1-hexene (GHSV 22500 h⁻¹; inlet hexene 3.0 wet mol %; S:C 4.6; Ni-com catalyst loaded 0.58 g; Nitrogen as a diluent; Total dry flow 43 mL min⁻¹; water flow 9.6 mL h⁻¹).

It is not surprising that a double bond compound such as hexene possesses a greater tendency to carbon formation in comparison to paraffins. The aromatic compound such as toluene may be worse than hexene for carbon deposition during steam reforming operation over nickel based catalyst. Nevertheless, Trimm [17-19] suggested that precious metals

such as platinum had a better quality than nickel in avoiding carbon formation, despite the fact that platinum was more susceptible to carbon monoxide poisoning.

As a result, a small amount of platinum (ca. 2 wt % as Pt) was deposited on to Ni-com catalyst (Chapter 4) and the composite catalyst was tested for the steam reforming of toluene for 24 hours. Results are shown in Figure 7.6.

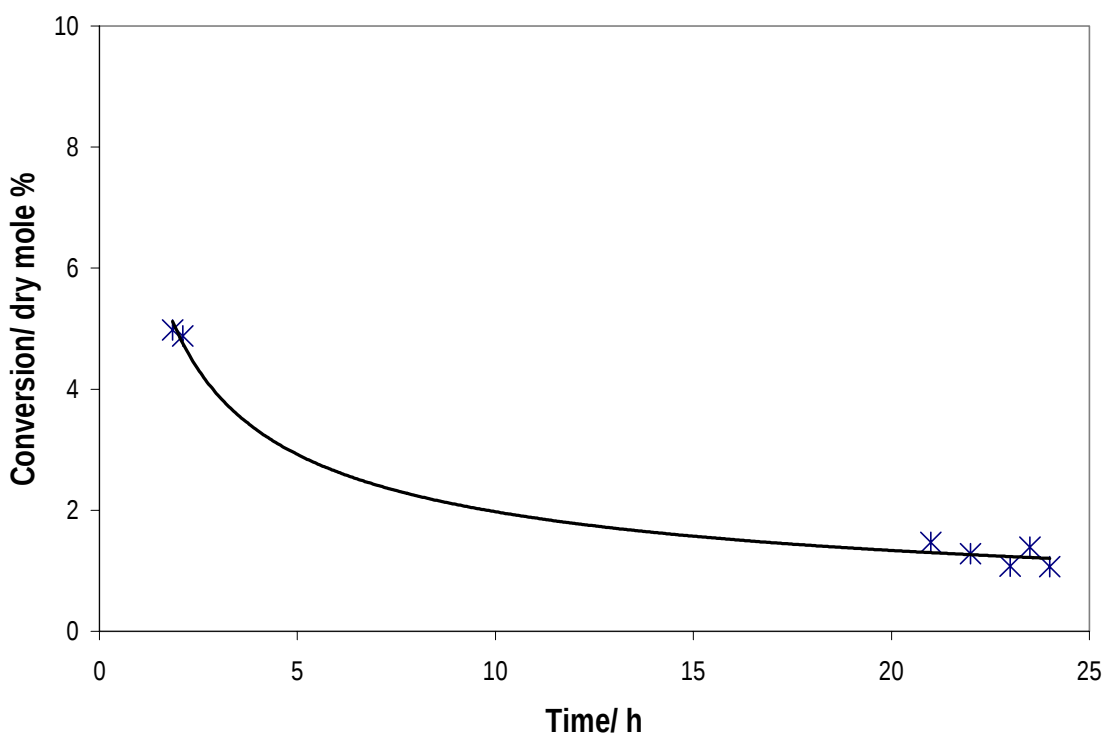


Figure 7.6 Stability test for steam reforming of toluene at 350 °C (GHSV 19700 h⁻¹; inlet toluene 1.2 wet mol %; S:C 3.2; Pt/Ni-com catalyst loaded 0.20 g; Nitrogen as a diluent; Total dry flow 57 mL min⁻¹; water flow 0.8 mL h⁻¹).

The observed initial conversion was low (ca. 5 %), and dropped dramatically to ca. 1% after 20 hours of operation.

For comparison, a similar experiment was done for normal octane as a representation of a straight alkane in gasoline. Figure 7.7 shows the observed results.

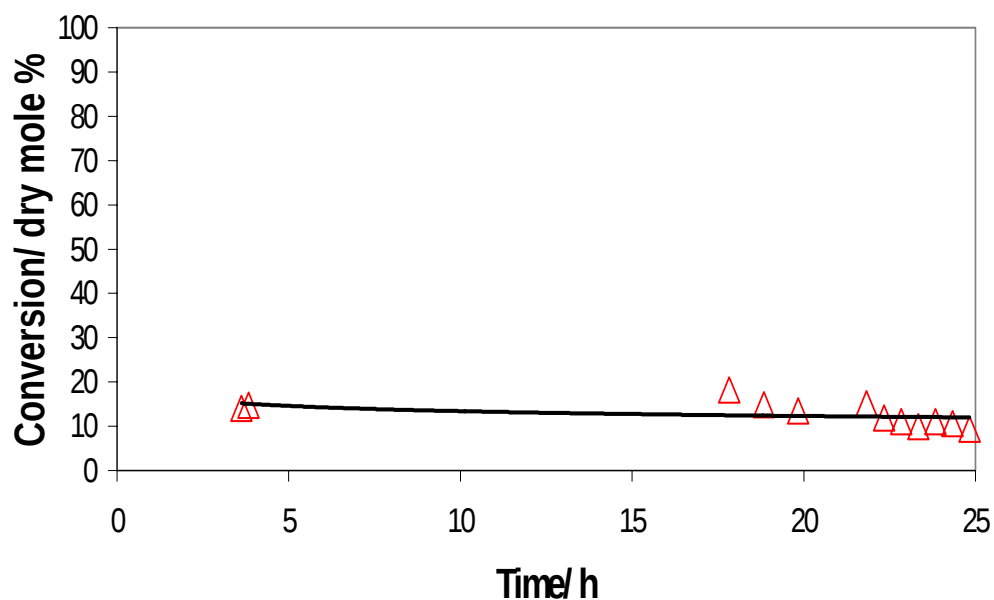


Figure 7.7 Stability test for steam reforming of octane at 350 °C (GHSV 19000 h⁻¹; inlet octane 1.0 wet mol %; S:C 3.0; Pt/Ni-com catalyst loaded 0.40 g; Nitrogen as a diluent; Total dry flow 108 mL min⁻¹; water flow 1.6 mL h⁻¹).

The observed overall conversion was about 15 %. As expected, octane conversion was more stable than toluene within 24 hours of operation. The conversion profile during the stability test was also consistent with the results of isooctane steam reforming profile over the Ni-com catalyst only, despite the fact that the former exhibited a lower overall conversion.

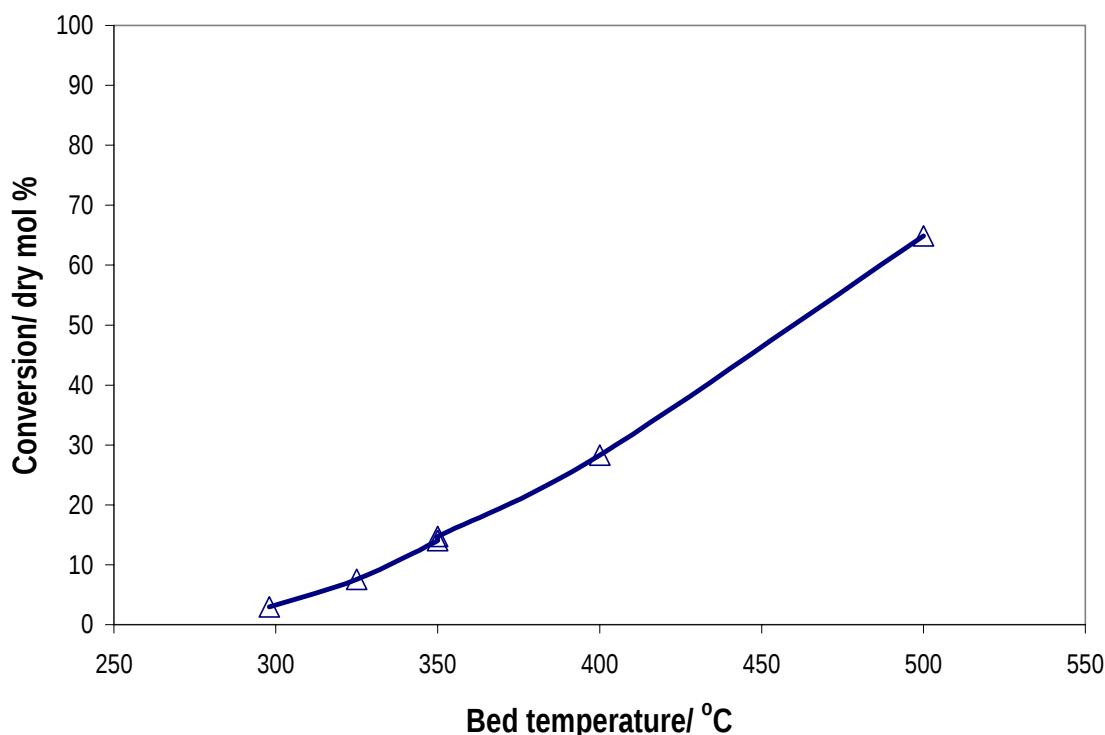


Figure 7.8 Conversion profile for the steam reforming of octane (GHSV 19000 h⁻¹; inlet octane 1.0 wet mol %; S:C 3.0; Pt/Ni-com catalyst loaded 0.40 g; Nitrogen as a diluent; Total dry flow 108 mL min⁻¹; water flow 1.6 mL h⁻¹).

Figure 7.8 shows the conversion profile for the steam reforming of octane as a function of bed temperatures.

As seen, the light out temperature was between 350 – 500 °C. No complete consumption of octane was observed even at temperatures as high as 500 °C.

Care was taken to maintain the inlet concentration of hydrocarbons to have the same amount of total carbon content. This was not always the case due to the experimental difficulties in handling various liquid hydrocarbons in saturators. As a result, besides conversion profiles for comparison of individual gasoline-like hydrocarbons, hydrogen yields measured as the amount of hydrogen produced over the total carbon fed into the reactor was also used as the basis of comparison. Figure 7.9 and 7.10 show the

comparison of conversion profile and hydrogen yield respectively for the individual hydrocarbons tested. Whilst isooctane, cyclohexane and hexene were tested over Ni-com catalysts, the comparison also incorporated the steam reforming of octane over a Pt/Ni-com catalyst. Bearing in mind that the rate of reaction for steam reforming of hydrocarbons over platinum was much less than that of over nickel based catalysts [20] and the bulk composition of a composite catalyst was ca. 98 wt % of Ni-com, it could be assumed that the major contributor for the steam reforming of octane came from the Ni-com content. Therefore, the comparison for the purpose of hydrocarbons scrutiny was justified.

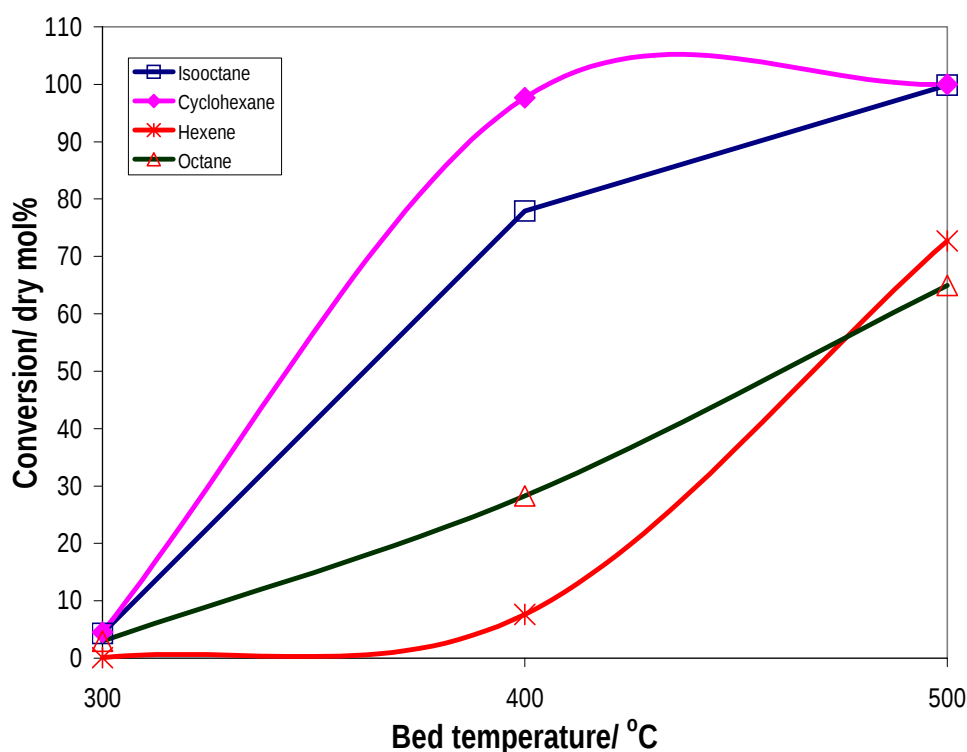


Figure 7.9 The conversion profile of various individual gasoline-like hydrocarbons (GHSV 19000 to 22500 h⁻¹; S:C = 3 to 4.5; Ni-com catalysts used except that Pt/Ni-com catalyst used for the steam reforming of octane).

As seen, the conversion was negligible for all hydrocarbons tested at 300 °C, however when the bed temperature was increased to 400 °C or above, cyclohexane exhibited the

highest conversion at elevated temperatures. At 500 °C, both cyclohexane and isooctane attained their full conversion.

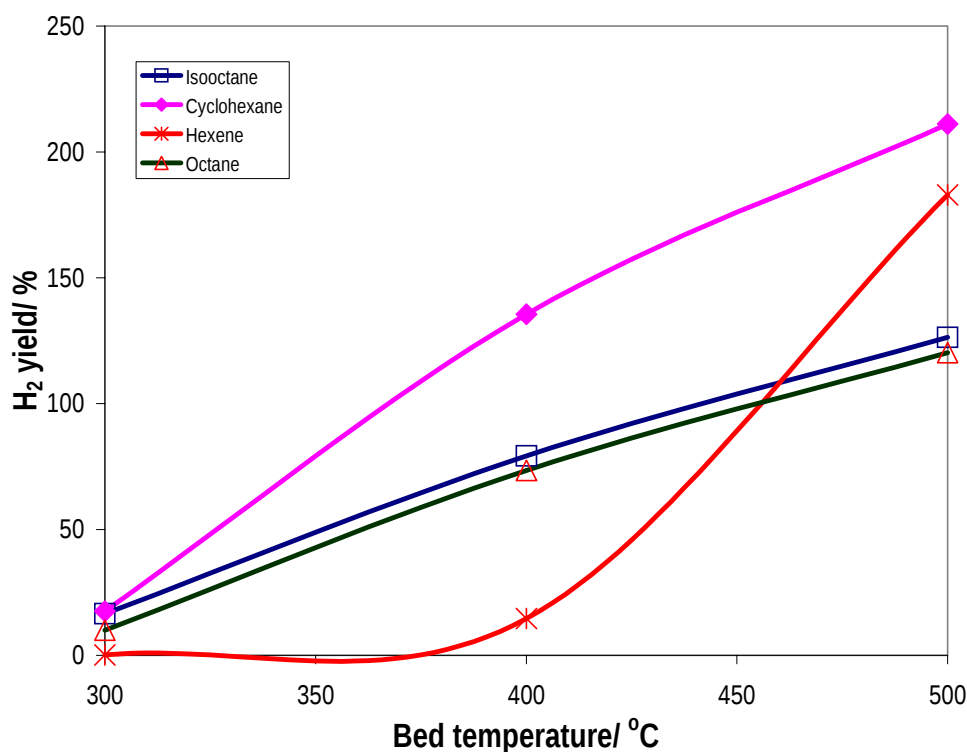


Figure 7.10 The hydrogen yield profile for various individual gasoline-like hydrocarbons (operating conditions were similar to Figure 7.9).

7.4 Conclusions

In conclusion, the results observed from the steam reforming of individual hydrocarbons experiments as well as the partial oxidation studies (Chapter 6) suggested that toluene and 1-hexene could not be used for the artificial gasoline formulation, due to their higher risk of carbon formation in comparison to isooctane, cyclohexane and octane. It is then intended to mix 8.33 % of cyclohexane, 58.34 % of isooctane and 33.33 % of octane on a volume basis as a final formula for the artificial gasoline. In relation to the results observed for the

partial oxidation experiments, an amount of hydrocarbons should be burned in such a way that the heat evolved from the exothermic reaction could increase the catalyst bed temperature from ambient to more than 400 °C in the context of autothermal reforming operation.

The steam reforming of artificial gasoline was then carried out and the results were reported in Chapter 8 in conjunction to the kinetic studies of steam reforming for isooctane and artificial gasoline.

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Chapter 8 Kinetics and mechanism of steam reforming of artificial gasoline

8.1 Introduction

The kinetics of steam reforming of artificial gasoline is required in order to be able to optimise operating conditions for the proposed autothermal reforming. Initial attempts involved studies of the kinetics of steam reforming of isooctane as a model for gasoline at three reaction temperatures at 310, 330, and 350 °C over a commercial nickel based catalyst. Reaction orders were determined and attempts were made to fit the data to an empirical power rate law and theoretical Langmuir-Hinshelwood (LH) models. The kinetic investigation was then continued for the steam reforming of artificial gasoline.

8.2 Literature review

Investigations on catalytic steam reforming commonly employ methane as hydrocarbon substrate. While many authors suggest that the reaction was first order with respect to methane, the data were not conclusive on the effect of steam on the reaction rate. Further discussion can be found elsewhere [1-3].

Little attention has been focused on the kinetics of steam reforming of higher hydrocarbons. Figueiredo [4] reported a rate order of 0.6 with respect to propylene and an activation energy of 67 kJ mole⁻¹ was found. Bhatta and Dixon [5, 6] observed zero order

with respect to n-butane and first order toward steam over a Ni/ γ -Al₂O₃ catalyst and an activation energy of 54 kJ mole⁻¹ was reported. However when α -Al₂O₃, UO₂, and 0.3% K supports were used instead of γ -Al₂O₃, the observed rate law was first order toward n-butane and -0.6 with respect to steam. The zero order with respect to cyclohexane and (0 – 1) order toward steam, with an activation energy of 96 kJ mole⁻¹, was reported by Balashova et al. over Ni/SiO₂ catalyst [7]. Kato and Ogino [8] observed zero order with respect to n-heptane and first order toward steam with an activation energy of 117 kJ mole⁻¹ over Ni/WO₃ catalyst. Tottrup [9] reported an order of (0.1 – 0.3) toward n-heptane, -0.2 with respect to steam, and 0.8 toward hydrogen with an activation energy corrected for pore diffusion of 67 kJ mole⁻¹. More recently, Wang and Gorte [10] observed activation energies of 65, 64, 61 and 85 kJ mole⁻¹ for the steam reforming of n-hexane, n-butane, ethane and toluene respectively over Pd/ceria catalysts, but no reaction orders were reported. Wang et al. [11] studied the kinetics of autothermal reforming for gasoline, regrettably, no reaction orders, nor activation energies were reported. Springmann et al. [12] reported isothermal kinetic experiments for liquid hydrocarbons in the context of autothermal reforming, but no kinetic expression was proposed.

It is clearly seen that, catalyst supports play an important role in determining the order of reaction of higher hydrocarbons steam reforming and the corresponding values of activation energies. Despite the fact that no conclusive agreement can be drawn with respect to the order of reaction toward steam, there is no doubt that orders of close to the zero with respect to higher hydrocarbons can be expected.

8.3 Kinetics of isooctane steam reforming

A commercial NiO/MgO based catalyst (Ni-com) was used in this study. The apparatus used, catalyst loading and activation testing are described in Chapter 3. Blank runs were performed using only a support (α -Al₂O₃) at a mild temperature (ca. 350 °C) and negligible activity was observed.

Preliminary experiments were then performed to test for pore and film diffusion. Four particle sizes of nickel catalyst of 180 – 212 microns, 250 – 300 microns, 300 – 425 microns, and 425 – 500 microns were tested under the standard operating conditions as reported in Table 8.1. No pore diffusion was evident as shown by Figure 8.1.

Even though all particle size ranges evaluated indicated absence of film diffusion, the size of 300 – 425 microns was chosen in order to minimise pressure drop across catalyst bed, especially when higher feed flow rates were used. The bigger size of 425 – 500 microns could be ground to 300 – 425 microns when required. Feed flow rates were then varied between 200 – 400 mL min⁻¹ STP, whilst space velocity and bed temperature were kept constant in accordance to Table 8.1. There was negligible film diffusion for flow rates in excess of 200 ml min⁻¹ as shown in Figure 8.2.

Table 8.1 Operating conditions for mass transport resistance elimination experiments

Description	Pore diffusion	Film diffusion
Catalyst loading, g	0.1	0.1 – 0.2
Reaction temperature, °C	350	350
Water feed rate, mL hr ⁻¹	2.31	2.31 – 4.63
Isooctane/N ₂ flow, mL min ⁻¹ (STP)	51.9	51.9 – 199.4
N ₂ diluent, mL min ⁻¹ (STP)	99.3	99.3 – 102.8
Inlet partial pressure of isooctane, kPa	1.1 ± 0.1	1.1 ± 0.1
Inlet partial pressure of steam, kPa	24.5 ± 0.4	24.5 ± 0.4
Total pressure, kPa	101.3	101.3
Total space velocity (GHSV), hr ⁻¹	134400	134400

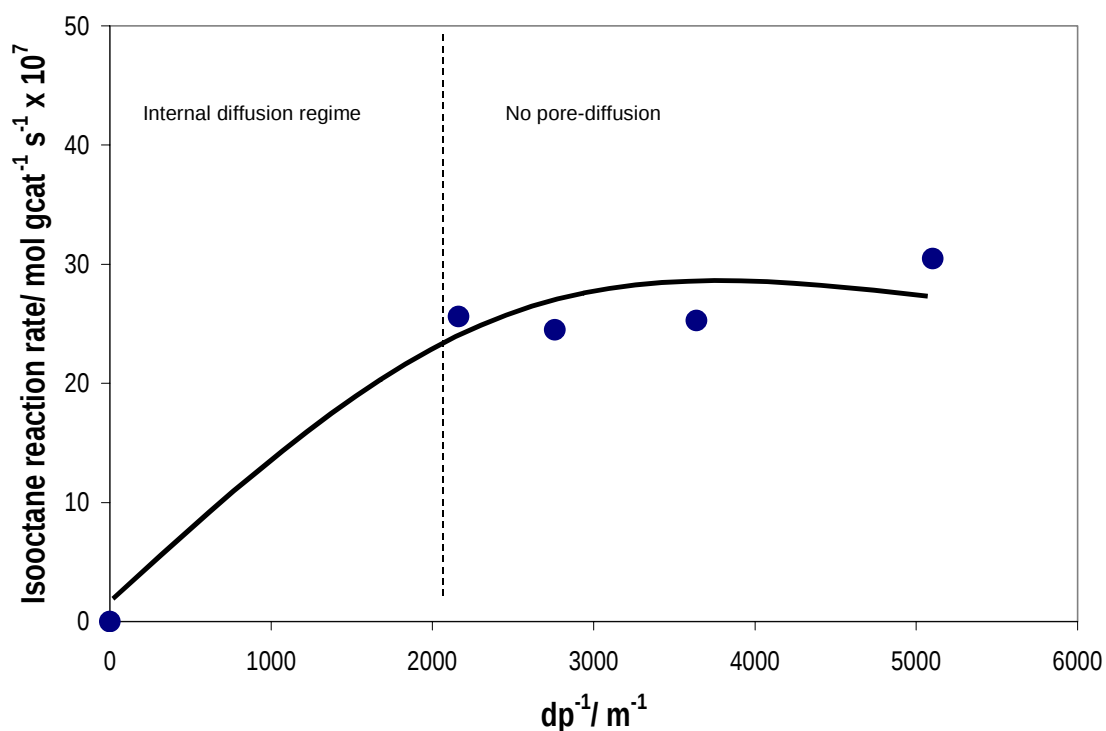


Figure 8.1 Pore diffusion experiment (Reduced Ni-com catalyst 0.1g; total flow 200 mL min⁻¹; inlet isooctane 1 wet %; S:C = 3:1; temperature 350 °C)

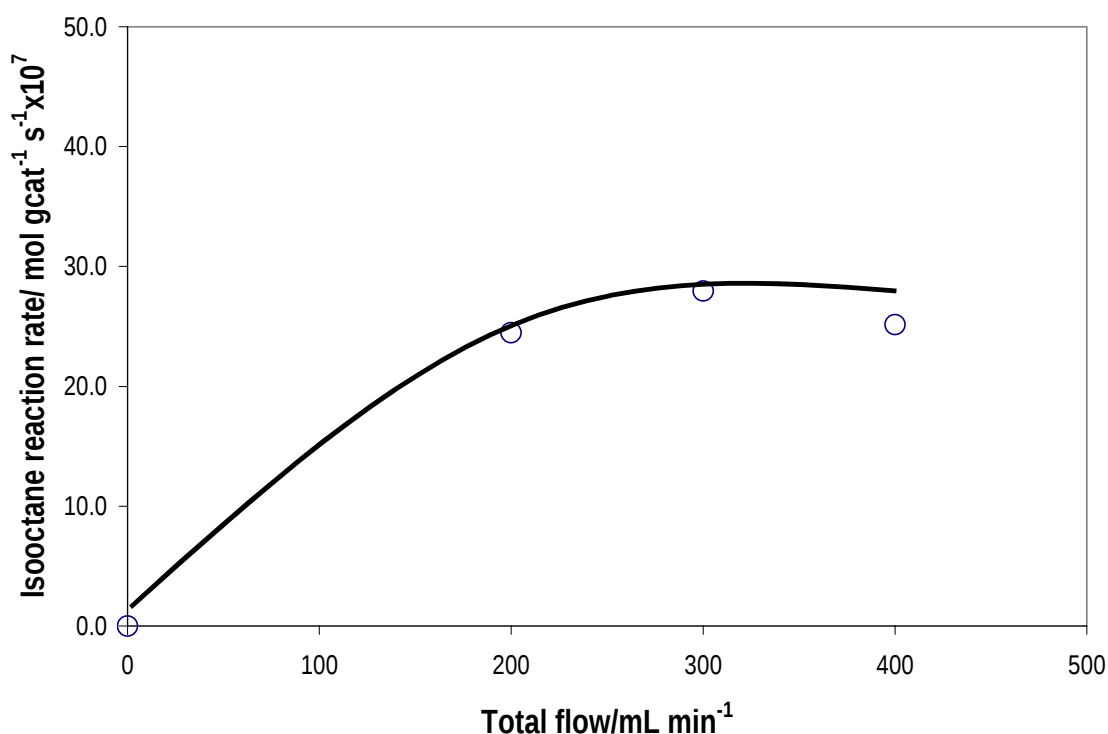


Figure 8.2 Film diffusion experiments (Reduced Ni-com catalyst 0.1 – 0.2 g; inlet isooctane 1 wet %; S:C = 3:0; GHSV 134400 h⁻¹; temperature 350 °C)

Experiments were undertaken by varying the partial pressure of all reactant simultaneously and measuring the rate of isooctane steam reforming. Nitrogen was used as a diluent. Details of experimental conditions are presented in Table 8.2 and results are provided in Table 8.3. The choice of experimental conditions was dictated by two constraints, namely a low value of isooctane vapour pressure at the selected saturator temperature of 20 °C, and steam : carbon ratios such that carbon deposition or re-oxidation of reduced-nickel would be avoided. As a result, isooctane feed concentrations of ca. 0.3 – 1.5 mol % (wet basis) and steam : carbon ratios of ca. 3 – 7 were used. Initial attempts were made to extend the range of steam : carbon ratios to ca. 8 – 9 in order to be able to utilise the method of excess steam for determining a reaction order of isooctane [13], but the reaction temperature was very difficult to control to within ca. 1°C. Values were erratic to

ca. 10 - 50°C against the set point due to an exothermic reaction of nickel oxidation, a condition which was unacceptable for kinetic experiments. Introduction of hydrogen to the feed to avoid catalyst oxidation at higher steam:carbon ratios was an unrealistic approach in the context of the manufacture of hydrogen on-board a vehicle.

Table 8. 2 Operating conditions for isooctane kinetic experiments

Description	Values
Catalyst loading, g	0.15– 0.20
Reaction temperature, °C	310,330,350
Water feed rate, mL hr ⁻¹	1.16 – 8.10
Isooctane/N ₂ flow, mL min ⁻¹ (STP)	50 – 200
N ₂ diluent, mL min ⁻¹ (STP)	0 – 325
Inlet partial pressure of isooctane, kPa	0.28 – 1.47
Inlet partial pressure of steam, kPa	6.15 – 56.9
Total pressure, kPa	101.3
Total space velocity (GHSV), hr ⁻¹	134400

The first series of experiments followed a Fibonacci Search [14], where isooctane partial pressure was kept constant at ca. 1 mol % (wet basis), while steam:carbon ratios were varied at 3, 4, and 5. Since this initial search showed a positive order to steam partial pressures, a higher steam:carbon ratio could be expected to increase the rate of steam reforming. Table 8.3 presents rate of isooctane steam reforming as a function of reaction temperature and reactants partial pressures.

Figures 8.3 shows the resultant plots of $\log_e (\ln)$ rate versus $\log_e (\ln)$ partial pressure of isooctane at a constant steam:carbon of ca. 3. Both factors (isooctane and steam partial

pressures) are seen to be influencing the rate. The reaction rate of isooctane increased slightly as the partial pressure of isooctane and steam was increased, indicating a reaction order of about 0.2. As expected, the reaction rate of isooctane increased as the temperature increased from 310 °C to 330 °C and 350 °C respectively.

Figure 8.4 shows the resultant plots of $\log_e (\ln)$ rate versus $\log_e (\ln)$ partial pressure of steam at a constant partial pressure of isooctane of 1.12 kPa. The isooctane consumption rate increased as a function of the partial pressure of steam over the range investigated, suggestion order with respect to steam of about 0.5.

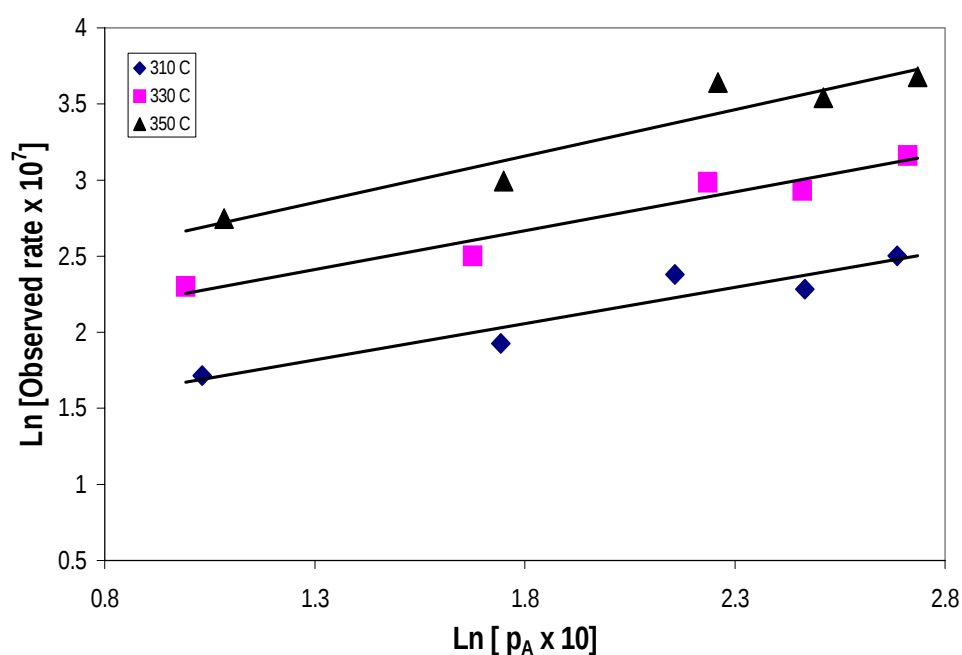


Figure 8.3 Rate of isooctane steam reforming ($\text{mol gcat}^{-1} \text{s}^{-1}$) vs. isooctane or steam partial pressure at a constant initial steam/carbon ratio of 3 (p_A = partial pressure of isooctane).

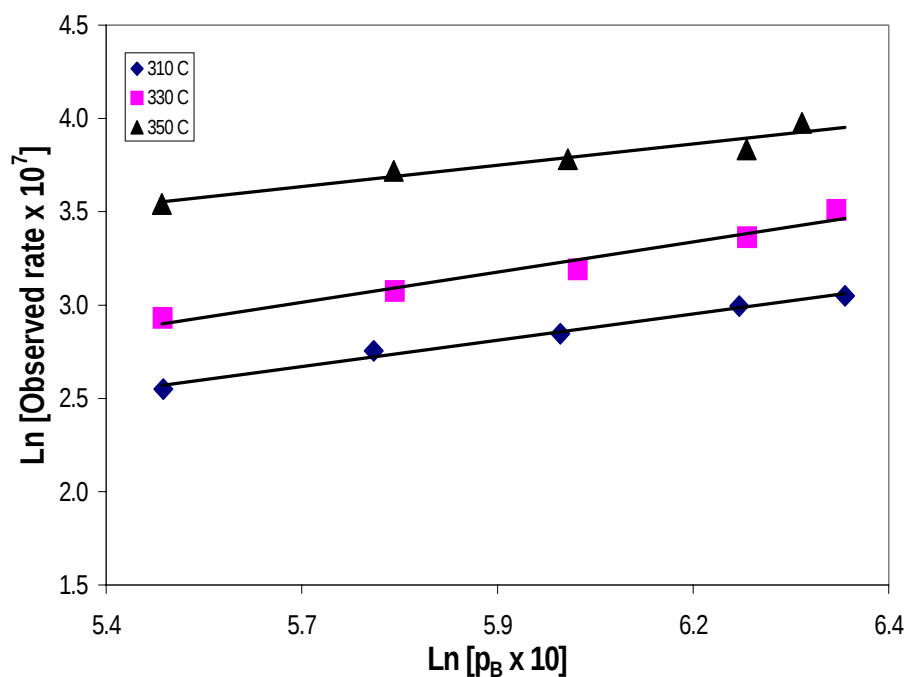


Figure 8.4 Rate of isooctane steam reforming (mol gcat⁻¹ s⁻¹) vs. steam partial pressure at a constant initial isooctane partial pressure (p_B = partial pressure of steam).

Table 8.3 Rates of isooctane steam reforming over a commercial nickel based catalyst

Temperature (°C)	Isooctane partial - pressure (kPa)	Steam partial- pressure (kPa)	Rate x 10 ⁷ (mol gcat ⁻¹ s ⁻¹)	Conversion, %
310	1.12	23.81	12.80	7.7
310	1.15	31.16	15.72	9.1
310	1.16	39.56	17.22	9.4
310	1.15	49.71	19.98	11.7
310	1.01	56.92	21.09	14.3
310	0.28	6.15	5.55	13.8
310	0.57	12.31	6.87	9.6
310	1.18	23.99	9.81	5.6
310	0.86	17.78	10.81	8.0
310	1.47	29.83	12.20	6.7
330	1.17	23.79	18.76	10.7
330	1.18	32.02	21.64	12.9
330	1.19	40.45	24.30	13.9
330	1.21	50.21	28.88	16.4
330	1.14	56.31	33.44	18.9

Temperature (°C)	Isooctane partial - pressure (kPa)	Steam partial- pressure (kPa)	Rate x 10 ⁷ (mol gcat ⁻¹ s ⁻¹)	Conversion, %
330	1.51	29.31	23.62	13.9
330	0.27	6.07	9.98	25.2
330	0.53	12.04	12.22	15.9
330	0.93	17.52	19.81	13.6
350	1.23	23.77	34.55	18.8
350	1.30	31.97	41.22	21.5
350	1.30	39.94	43.89	22.7
350	1.35	50.18	46.25	23.3
350	1.27	53.86	53.32	31.4
350	1.54	29.84	39.64	17.2
350	0.96	17.76	38.15	24.2
350	0.30	6.14	15.60	35.1
350	0.57	12.04	19.98	23.6

8.3.1 Power law modelling of the kinetic data

The data (Table 8.3) were fitted to a power rate model and parameter estimates were based on the power law kinetic having the form

$$r = k p_A^a p_B^b \quad (8.1)$$

where r is the rate of isooctane steam reforming (mol gcat⁻¹ s⁻¹),

k is the pseudo rate constant (mol gcat⁻¹ s⁻¹ kPa^{-(a + b)}),

p_A and p_B are the partial pressures of isooctane and steam respectively, and

a and b are the reaction orders with respect to isooctane and steam respectively.

Non-linear least-squares were used to estimate reaction orders, k_0 (frequency factor) and E (activation energy) by the use of an algorithm outlined by Fogler [13] for the first order reaction and also as suggested by Elnashaie et al. using the approach of so-called 4-parameter estimates [1]. In this case, initial estimates of k_0 and E found by a linearised least squares analysis were employed to solve the expanded form of equation (8.1) :

$$r = k_0 e^{-E/(RT)} p_A^a p_B^b \quad (8.2)$$

The procedure involves minimisation of the sum of the squared differences of the measured reaction rate and the calculated reaction rate having the form

$$\sigma^2 = \frac{\sum_{i=1}^N (r_{im} - r_{ic})^2}{(N - P - 1)} \quad (8.3)$$

Where N is the number of runs,

P is the number of parameters to be determined,

r_{im} is the measured reaction rate for run i ,

r_{ic} is the calculated reaction rate for run i .

Calculations are performed with the aid of SOLVER, a built-in subroutine provided by Microsoft Excel. All parameters found by linearised least squares (not reported) are used as initial estimates. The results are presented in Table 8.4.

Table 8.4 Estimates of parameters for isooctane steam reforming (non-linear least squares)

Parameter	Unit	4 - parameter estimates (k_0 , E , a , b)
k_0	$\text{mol gcat}^{-1}\text{s}^{-1} \text{ kPa}^{-0.71}$	$0.0026(\pm 0.0001)$
E	kJ mol^{-1}	$44.0(\pm 2.2)$
a (isooctane order)		$0.17(\pm 0.01)$
b (steam order)		$0.54(\pm 0.03)$

() : Uncertainty

The activation energy is lower than the value of 67.8 kJ mol^{-1} reported by Tottrup [9] for the steam reforming of n-heptane over Ni/MgO catalyst. Examination of activation energies reported by Rostrup-Nielsen [2, 3] and Tottrup [9] for the steam reforming of various hydrocarbons over nickel based catalysts as well as incorporating the present result revealed that the trend of values was decreasing as the carbon number increased as shown in Figure 8.5.

The observed reaction order with respect to isooctane is consistent with the suggestion of Rostrup-Nielsen [2, 3] that, for butane and other higher hydrocarbons, the orders tended to approach zero. Figure 8.6 shows a reasonable agreement between observed rate and predicted rate.

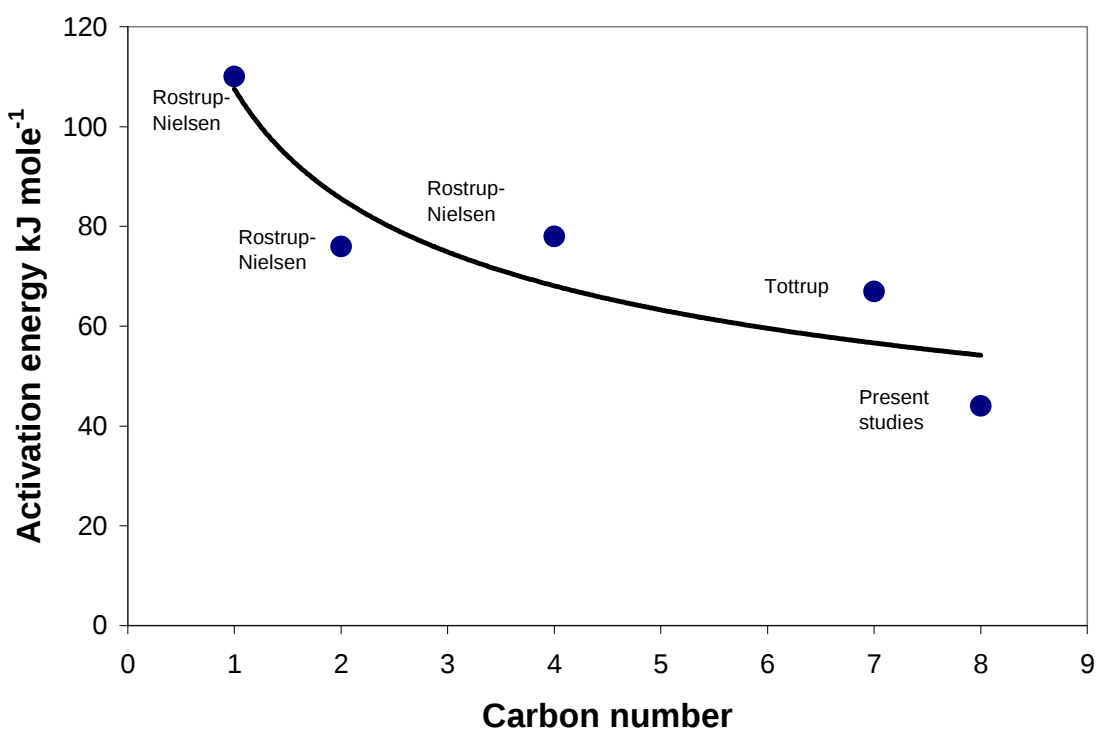


Figure 8.5 Activation energies of various paraffins over Ni/MgO catalysts

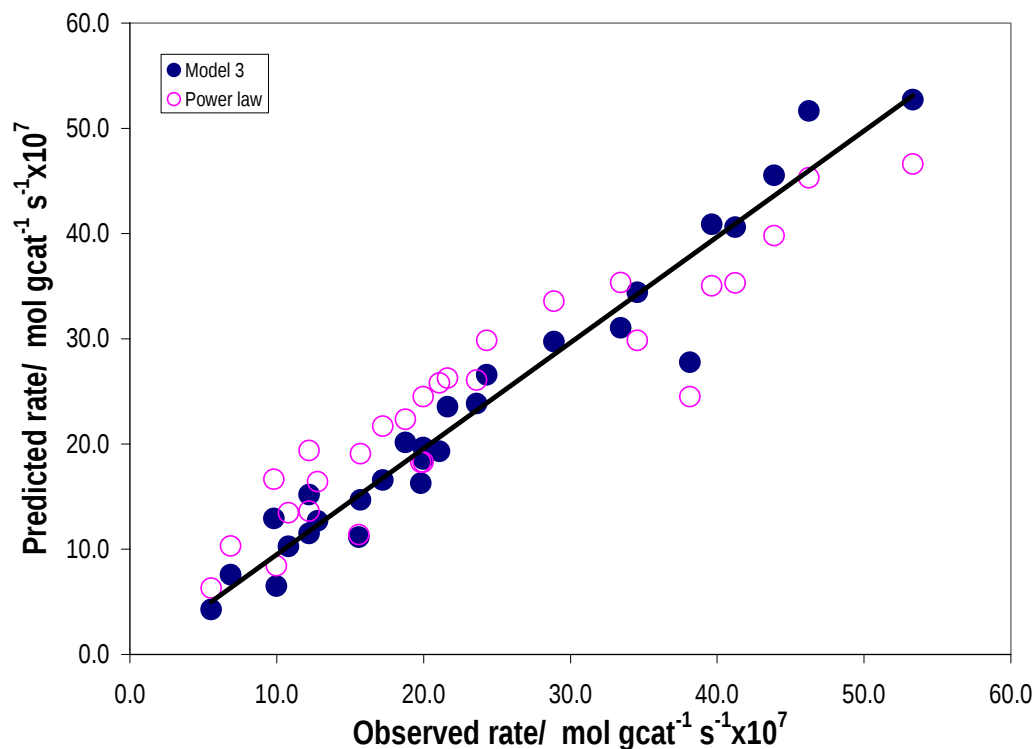


Figure 8.6 Predicted (Langmuir-Hinshelwood Model 3 and Power law) versus observed rate for isooctane steam reforming (non-linear least squares with 4-parameter estimates).

8.3.2. Mechanistic modelling of the kinetic data

In order to proffer a plausible mechanism for the reaction, rate data were fitted 6 different Langmuir-Hinshelwood and Eley-Rideal models, as displayed in Table 8.5. The accompanying remarks illustrate the key features of each mechanistic proposition. While there is an implicit mechanism associated with each kinetic model, the fitting of data to a model does not constitute proof of a mechanism. The same fit of the data can be obtained from two different models representing completely different mechanisms. As a result, a thermodynamic adequacy test is very important [15, 16].

Table 8.5 Theoretical reaction rate models

No.	Model	Remarks
1	$\frac{k_{rxn} p_A p_B}{(1 + K_A p_A + K_B p_B)^2}$	Molecular adsorption of both isooctane (A) and steam (B) on the same site followed by bimolecular surface reaction r.d.s.
2	$\frac{k_{rxn} p_A p_B}{(1 + K_A p_A)(1 + K_B p_B)}$	Dual-site with associative adsorption of isooctane (A) and steam (B)
3	$\frac{k_{rxn} \sqrt{p_A p_B}}{(1 + \sqrt{K_A p_A})(1 + \sqrt{K_B p_B})}$	Dual-site with dissociative adsorption of isooctane(A) and steam (B)
4	$\frac{k_{rxn} \sqrt{p_A p_B}}{(1 + \sqrt{K_A p_A + K_B p_B})^2}$	Single-site with dissociative adsorption of isooctane (A) and molecular adsorption of steam (B) followed by bimolecular surface reaction r.d.s.
5	$\frac{k_{rxn} p_A p_B}{1 + K_A p_A}$	Eley-Rideal model with associative adsorption of isooctane (A) with steam (B) in gas phase
6	$\frac{k_{rxn} \sqrt{p_A p_B}}{1 + \sqrt{K_A p_A}}$	Eley-Rideal model with dissociative adsorption of isooctane (A) with steam (B) in gas phase

As reported in Table 8.6, models 1-4 gave positive parameter estimates. Of the remaining models which employed Eley-Rideal mechanism, all gave negative values for one or more of the coefficients and hence were deemed inadequate mechanisms

Table 8.6 Parameter estimates of LH models *)

Model No.	Temp. (°C)	k_{rxn}	K_A	K_B	SSE
1	310	1.143E-06	3.230	0.021	1.80
	330	1.988E-06	2.815	0.040	8.27
	350	2.901E-06	2.246	0.046	19.72
2	310	2.842E-05	0.965	10.473	24.40
	330	3.817E-05	0.851	9.285	34.16
	350	5.130E-05	0.630	8.600	52.37
3	310	1.078E-05	0.983	109.683	4.63
	330	1.460E-05	0.876	86.204	8.48
	350	1.917E-05	0.769	55.153	32.36
4	310	1.311E-04	1997.238	0.219	2.08
	330	2.133E-04	1759.448	0.314	8.70
	350	3.075E-04	1271.281	0.352	32.34
5	310	7.017E05	-1.751		3.65E+36
	330	-5.369E07	637.527		1.04E+13
6	310	4.194E05	-0.188		N/A

*) A : isooctane; B : steam; N/A : Not Available

Models 1 – 4 were then assessed against the Boudart-Mears-Vannice [15, 16] guidelines in order to test their thermodynamic adequacy. This criterion is given by:

$$10 < -\Delta S_{exp} < 12.2 - 0.0014 \Delta H_{exp} \quad (8.3)$$

where

$$\ln K = -\Delta H/(RT) + \Delta S/R \quad (8.4)$$

Parameter estimates are presented in Table 8.7, while the activation energy is reported in Table 8.8. For model 1, 2, 3 and 4, the adsorption constants of isooctane (K_A) satisfied the van't Hoff's relation, but the steam adsorption constant (K_B) for models 1 and 4 increased

as the reaction temperature increased. This phenomenon is not uncommon as reported by Xu and Froment [17] for the steam reforming of methane.

Table 8.7 Estimates of models 1 to 4 for BMV guidelines

Parameter				Corr. Coeff. (r^2)	- $\Delta S > 10$	- $\Delta S < (12.2 - 0.0014 \Delta H)$
ΔH_A , J mol ⁻¹	Model 1	-27357		0.98		
	Model 2	-32050		0.94		
	Model 3	-18480		0.99		
	Model 4	-33927		0.93		
ΔS_A , J mol ⁻¹ K ⁻¹	Model 1	-37.0		0.98	37 > 10	37 < 50.5
	Model 2	-55.0		0.94	55 > 10	55 < 57.1
	Model 3	-31.8		0.99	31.8 > 10	31.8 < 38.1
	Model 4	5.3		0.93	No	-5.3 < 59.7
ΔH_B , J mol ⁻¹	Model 1	59064		0.89		
	Model 2	-14910		0.99		
	Model 3	-51712		0.96		
	Model 4	35886		0.93		
ΔS_B , J mol ⁻¹ K ⁻¹	Model 1	69.9		0.89	No	Borderline
	Model 2	-6.1		0.99	No	6.1 < 33.1
	Model 3	-49.3		0.96	49.3 > 10	49.3 < 84.6
	Model 4	49.2		0.93	No	-49.2 < -38

A : isooctane; B : steam

Table 8.8 Estimate of activation energy for models 1 - 4

1/T, K ⁻¹	-Ln k_{rxn}				E, kJ mol ⁻¹				r^2			
	M1	M2	M3	M4	M1	M2	M3	M4	M1	M2	M3	M4
0.00172	13.68	10.47	11.44	8.94	70.4	44.6	43.5	64.4	0.990	0.999	0.999	0.996
0.00166	13.13	10.17	11.13	8.45								
0.00161	12.75	9.88	10.86	8.09								

M : Model

All rate constants exhibited Arrhenius-dependency as can be seen in Table 8.8 . The expected error range for the reaction rate calculated as described in Adesina's work [18] was 1.7 – 2.5 %. Therefore only model 3 satisfied statistical and thermodynamic scrutiny. Figure 8.6 depicted a reasonable agreement between observed and predicted rates for model 3.

Model 3 suggests that the reaction probably proceeds via dissociative adsorption of isooctane to a site different from that on which steam dissociatively chemisorbs. Spectroscopic studies of transient metal surfaces [19-22] reveal the presence of metal-hydroxyl bonds at temperatures above 127 °C under hydrogen-rich conditions. Indeed, since hydrogen frequently exists as H adatoms on the group VIII metals, it is conceivable that H₂O would split into surface H and OH species upon chemisorption under steam reforming conditions. However, due to steric effects and the electron-donating capacity, isooctane would preferably adsorb on contiguous electron-deficient sites, fragmenting, in the process, to smaller C_aH_b entities (a,b <8).

Dissociative adsorption of C₂₊ hydrocarbons has been observed with different metal oxides [23-30]. This provides precedence for the dual-site adsorption mechanism implicated by the adequacy of model 3.

To ascertain the validity range of the kinetic expressions as proposed by model 3, a rigorous error analysis is incorporated by carrying out a residual analysis. If the model is adequate, the residuals should be structureless [31]. Figure 8.7 shows plot of residuals

versus fitted values of reaction rates of model 3 ($\text{mol gcat}^{-1} \text{s}^{-1} \times 10^7$). It is seen that there is no obvious patterns.

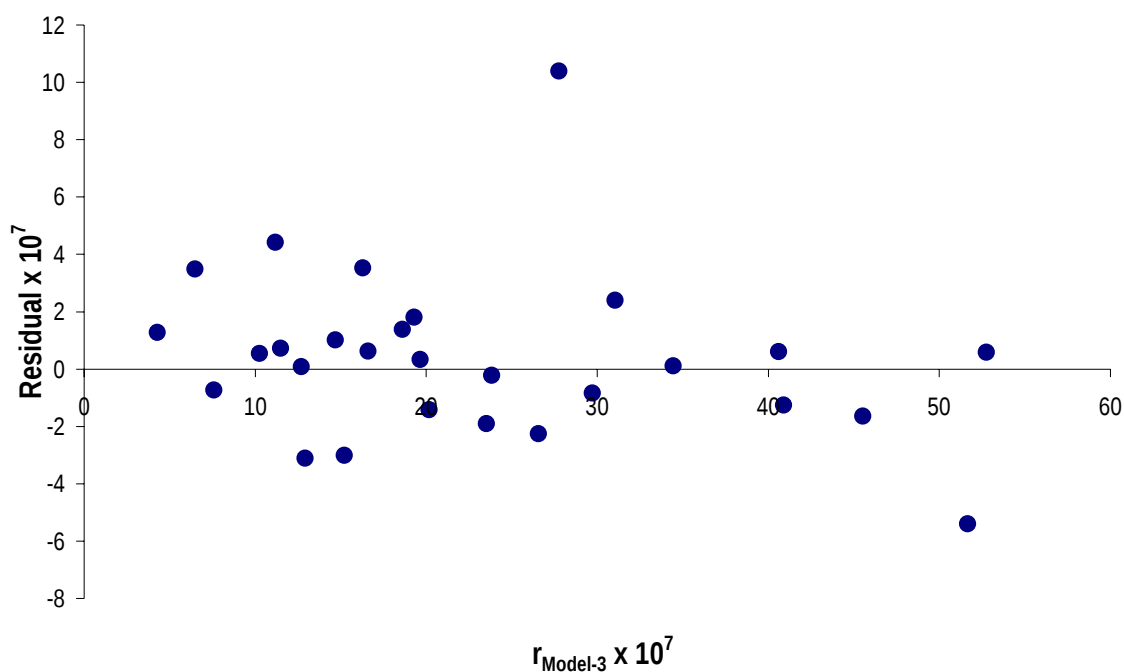


Figure 8.7 Plot of residuals versus fitted values

8.3.3 The effect of carbon dioxide on the kinetics of isooctane steam reforming

Figure 8.8 shows the effect of the addition of carbon dioxide in feed. As expected, at low temperature, carbon dioxide caused no changes in reaction rate and in hydrogen product concentration. As a result, no further kinetic studies were attempted. This finding was in agreement with previous kinetic studies for the steam reforming of light hydrocarbons [32].

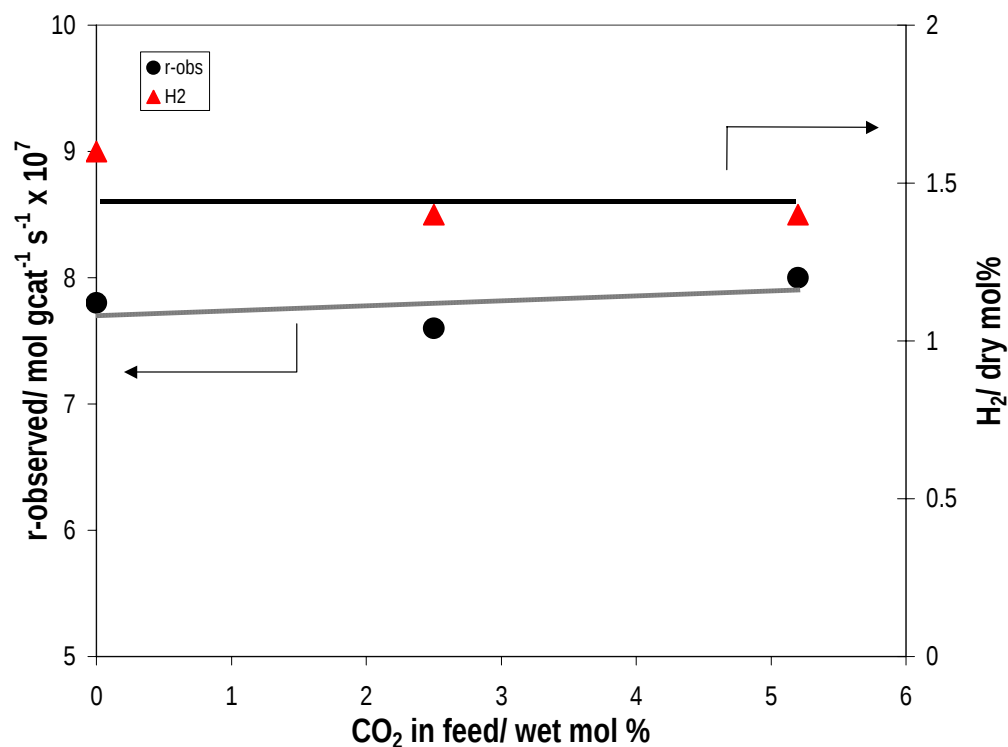


Figure 8.8 Effect of CO₂ in feed (Reduced Ni-com catalyst 0.15 g; GHSV 134000 h⁻¹; inlet isooctane 1 wet %; S:C = 3.2 :1; temperature 350 °C)

8.3.4 Summary

In summary, the kinetic of isooctane steam reforming over a nickel based catalyst has been studied at atmospheric pressure over a relatively wide temperature range (310 – 350 °C). A power rate law of the following form fits the experimental data well :

$$r = k_0 e^{\frac{-44,000 \frac{\text{J}}{\text{mol}}}{RT}} p_{\text{C}_8\text{H}_{18}}^{0.17} p_{\text{H}_2\text{O}}^{0.54} \quad (8.5)$$

Fitting the experimental data to the Langmuir-Hinshelwood kinetics shows that the rate determining step in the steam reforming of isooctane involves the reaction between dissociatively adsorbed species of isooctane and steam. The resulting activation energy is

comparable to the steam reforming of heptane over Ni/MgO catalyst as reported by Tottrup [9].

8.4 Kinetics of the steam reforming of artificial gasoline

8.4.1 Stability test for the steam reforming of mixed cyclohexane, isooctane and octane

Studies of the steam reforming of individual gasoline-like hydrocarbons has been carried out (Chapter 7). The results revealed that only cyclohexane, isooctane and octane were feasible as components for the artificially mixed gasoline based on the severity of carbon deposition.

It was decided to mix 8.33 % of cyclohexane, 58.34 % of isooctane and 33.33 % of octane on a volume basis, as a simplification of a typical Australian gasoline composition identified by Duffy and Nelson [33]. Isooctane (boiling point 98 - 99°C) and cyclohexane (boiling point 80 - 82°C) were put in the first saturator, whilst octane (boiling point 125 - 127°C) was poured into second saturator. The third saturator which was only loaded with glass packing and was used as a stabiliser vessel.

Initial experiments involved a 24 hour stability test as shown in Figure 8.9.

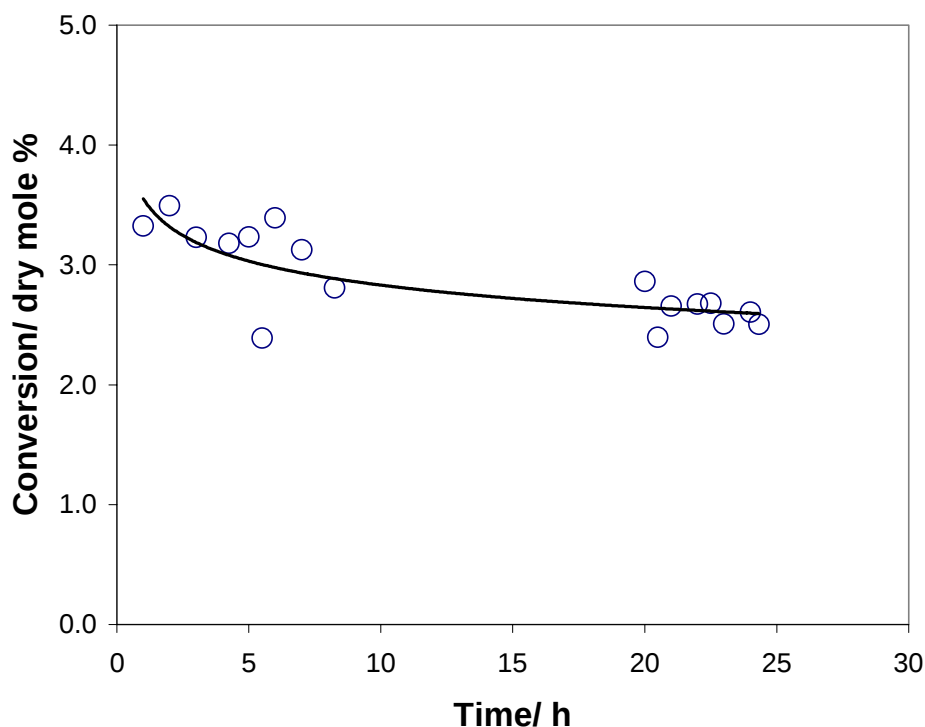


Figure 8.9 Stability test for the steam reforming of artificial gasoline at 350 ° C (GHSV 132200 h⁻¹; Ni-com catalyst 0.15 g; S:C = 2.9:1; inlet total hydrocarbons 1.8 wet %; inlet total dry flow 182.5 mL min⁻¹).

Testing conditions were similar to those of kinetic of isooctane steam reforming.

As seen in Figure 8.9, the initial overall conversion was low in comparison to the steam reforming of individual hydrocarbons (Chapter 7). Nevertheless, the conversion was stable at ca. 2.7 % after 20 hours of operation. The catalyst was then re-oxidised and re-reduced using similar techniques as previously described in Chapter 7 in order to investigate the possibility of carbon formation on the catalyst surface. The experiment was started again under the same conditions as above, but a few hours of operation revealed that the conversion was stable in the vicinity of about 2.7 %.

8.4.2 Conversion test for the steam reforming of mixed isooctane and octane

An attempt was then made to investigate the steam reforming of a mixture of isooctane and octane with the same isooctane to octane ratio as used in the previous run. Figure 8.10 shows the results.

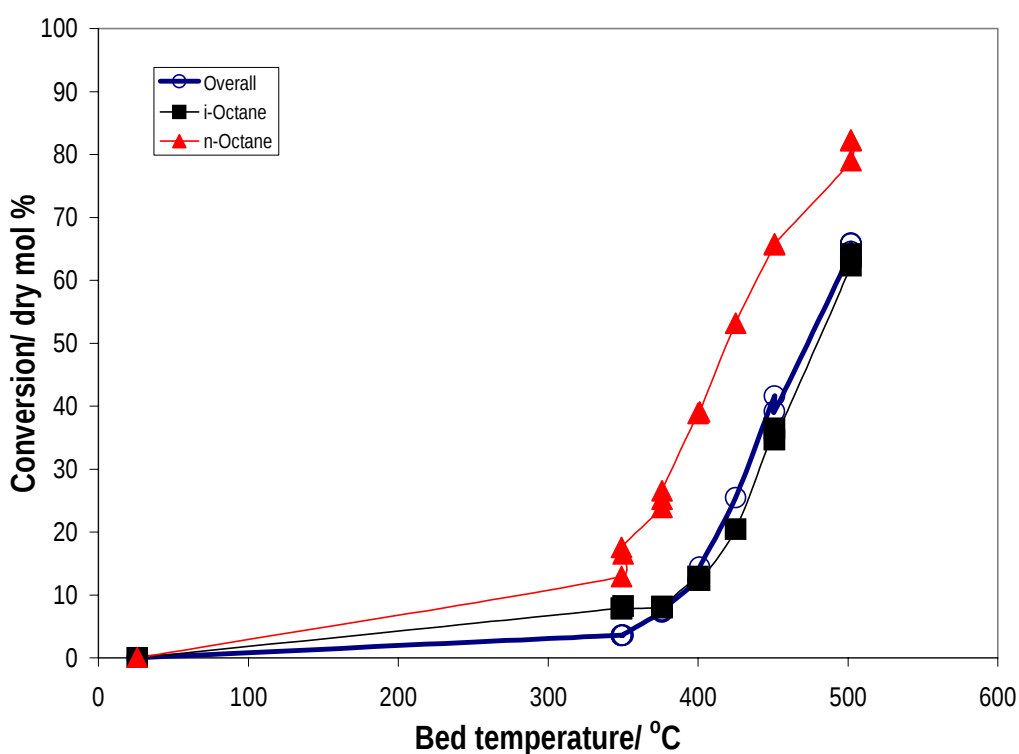


Figure 8.10 Conversion profile for the steam reforming of the mixture of isooctane and octane (GHSV 133800 h⁻¹; Ni-com catalyst 0.15 g; S:C = 3.5:1; inlet isooctane 1.3 wet %; inlet octane 0.3 wet %; total inlet dry flow 165 mL min⁻¹; Water flow 6.5 mL min⁻¹).

It is apparent that, the overall conversion lay between the individual curves for octane and isooctane, however, as expected, the overall conversion was closer to isooctane since the inlet concentration of isooctane was higher.

8.4.3 Conversion test for the steam reforming of individual hydrocarbons

Additional runs were conducted to test individual hydrocarbons. Experiments were sequentially carried-out as summarised in Table 8.9 while Figure 8.11 attests the data reproducibility.

Table 8.9 Experimental sequences for the steam reforming of octane and isooctane

Experiment	Description	Process conditions
1 st	Octane (Run1)	GHSV 132600 h ⁻¹ ; Ni-com 0.15 g; S:C=3.2:1; inlet octane 0.8 wet %; inlet dry flow 225 mL min ⁻¹ ; inlet water flow 3.5 mL h ⁻¹
2 nd	i-Octane (Run 1)	GHSV 136000 h ⁻¹ ; S:C = 2.8:1; Ni-com catalyst 0.15 g; inlet isooctane 1.1 wet %; total dry flow 232 mL min ⁻¹ ; inlet water flow 3.5 mL min ⁻¹
3 rd	Octane (Run 2)	GHSV 133300 h ⁻¹ ; Ni-com catalyst 0.15g; S:C 3.7:1; inlet octane 0.8 wet %; inlet dry flow 226 mL min ⁻¹ ; inlet water flow 3.5 mL h ⁻¹
4 th	i-Octane (Run 2)	GHSV 136000 h ⁻¹ ; Ni-com catalyst 0.15 g; S:C = 2.8:1; inlet isooctane 1.1 wet %; inlet dry flow 232 mL min ⁻¹ ; inlet water flow 3.5 mL h ⁻¹
5 th	i-Octane (Run 3)	GHSV 136000 h ⁻¹ ; Ni-com catalyst 0.15 g; S:C = 2.8:1; inlet isooctane 1.1 wet %; inlet dry flow 232 mL min ⁻¹ ; water flow 3.5 mL h ⁻¹

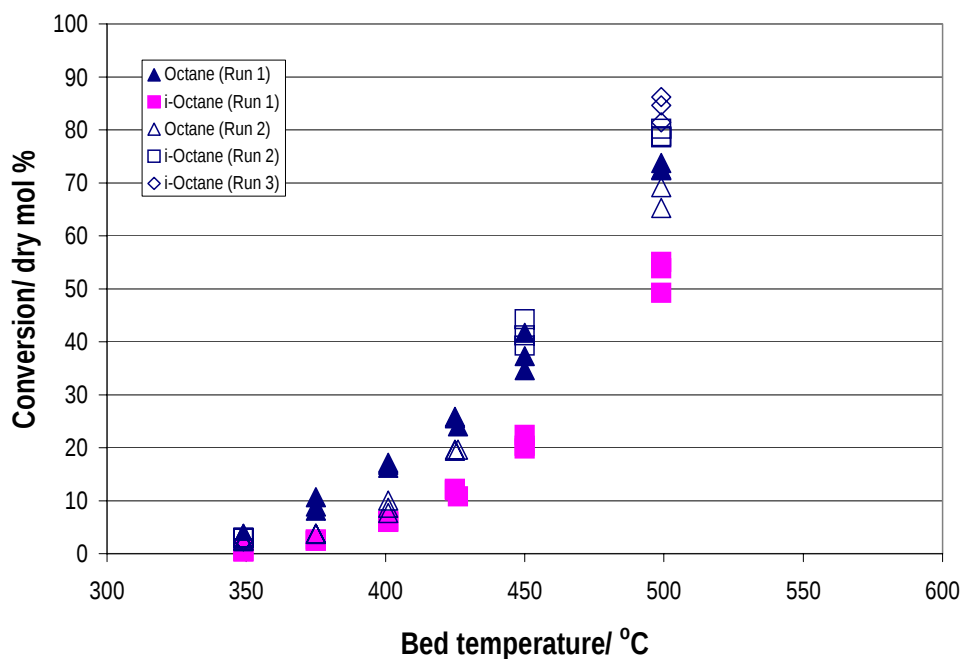


Figure 8.11 Reproducibility tests for the individual steam reforming of octane and isooctane (Process conditions as displayed by Table 8.9)

As seen in Figure 8.10 and Figure 8.11, a series of stability and consistency tests between a mixed octane and isooctane as well as two individual hydrocarbons over the same catalyst sample proved that the conversion profiles were reproducible. As a result, kinetic experiments for the artificial gasoline were feasible. It was decided to increase the temperature range to 375 – 425 °C or higher than the temperature range employed for the kinetic of single hydrocarbon, in order to attain the overall conversion between 10 – 20 %.

The kinetic studies were carried out at 7 different compositions. Hydrocarbons and steam partial pressures were varied simultaneously. Bearing in mind that the studies involving multi component hydrocarbons exhibiting competitive adsorption among species involved, a kinetic expression based on Langmuir-Hinshelwood for 5 parameters (k_{rxn} , K_A , K_B , K_C and K_D), would statistically require at least $2 \times 5 + 1$ [18] different feed compositions. This is

beyond the capacity of the experimental rig using saturators. Therefore, it was decided to introduce the concept of an effective hydrocarbon partial pressure by employing the following equation:

$$p_{he} = \sum_{i=1}^n p_{hi} \times \frac{\sum_{i=1}^n (Y_i M_i)}{\sum_{i=1}^n M_i} \quad (8.6)$$

Where p_{he} = effective partial pressure of artificial gasoline, kPa

p_{hi} = individual partial pressure of hydrocarbon, kPa

Y_i = individual mole fraction of hydrocarbon

M_i = individual molecular weight of hydrocarbon, g mole⁻¹

Table 8.10 shows experimental conditions for kinetic measurements of artificial gasoline.

Table 8.10 Experimental conditions for kinetic measurements of artificial gasoline

T, °C	p_{he} , kPa	p_s , kPa	r-obs. x 10 ⁷ (mol gcat ⁻¹ s ⁻¹)
374	0.016135	38.85	16.80
374	0.016135	38.85	18.04
375	0.016135	38.85	18.36
401	0.016135	38.85	39.37
401	0.016135	38.85	38.01
402	0.016135	38.85	34.88
425	0.016135	38.85	58.44
425	0.016135	38.85	53.98
425	0.016135	38.85	57.58
375	0.007232	64.26	17.37
374	0.007232	64.26	17.93
374	0.007232	64.26	17.46
400	0.007232	64.26	31.58
400	0.007232	64.26	32.09
399	0.007232	64.26	34.00

T, °C	p _{he} , kPa	p _s , kPa	r-obs. x 10 ⁷ (mol gcat ⁻¹ s ⁻¹)
425	0.007232	64.26	54.18
426	0.007232	64.26	56.00
425	0.007232	64.26	55.93
374	0.011784	51.88	21.12
374	0.011784	51.88	20.71
373	0.011784	51.88	21.32
400	0.011784	51.88	38.93
400	0.011784	51.88	39.32
400	0.011784	51.88	39.76
425	0.011784	51.88	63.84
425	0.011784	51.88	65.12
425	0.011784	51.88	63.22
375	0.015158	46.70	16.92
374	0.015158	46.70	17.18
375	0.015158	46.70	15.83
399	0.015158	46.70	31.12
400	0.015158	46.70	31.60
400	0.015158	46.70	31.48
425	0.015158	46.70	56.07
425	0.015158	46.70	55.26
425	0.015158	46.70	56.15
374	0.000998	20.97	11.29
374	0.000998	20.97	11.88
374	0.000998	20.97	11.63
400	0.000998	20.97	21.77
400	0.000998	20.97	18.88
400	0.000998	20.97	22.17
426	0.000998	20.97	32.06
425	0.000998	20.97	33.11
425	0.000998	20.97	33.69
374	0.022045	37.92	14.70
374	0.022045	37.92	13.81
374	0.022045	37.92	13.96
400	0.022045	37.92	26.79
401	0.022045	37.92	27.24
401	0.022045	37.92	28.30
426	0.022045	37.92	41.29
426	0.022045	37.92	45.52

T, °C	p _{he} , kPa	p _s , kPa	r-obs. x 10 ⁷ (mol gcat ⁻¹ s ⁻¹)
425	0.022045	37.92	46.61
374	0.011336	61.74	10.05
373	0.011336	61.74	12.34
400	0.011336	61.74	23.75
400	0.011336	61.74	24.14
400	0.011336	61.74	24.96
425	0.011336	61.74	42.60
425	0.011336	61.74	42.55
425	0.011336	61.74	45.08
375	0.013359	38.60	11.84
374	0.013359	38.60	12.72
401	0.013359	38.60	29.21
401	0.013359	38.60	28.29
401	0.013359	38.60	27.85
426	0.013359	38.60	51.35
425	0.013359	38.60	46.97
426	0.013359	38.60	44.89

The data were then fitted to a power law model given by

$$(-r) = 0.291 \exp \frac{-66,800 \frac{\text{J}}{\text{mol}}}{RT} p_{he}^{0.08} p_s^{0.23} \quad (8.7)$$

where (-r) = rate of artificial gasoline consumption, mol gcat⁻¹ s⁻¹.

As expected, the reaction order with respect to hydrocarbons partial pressure tended to approach zero whilst the larger order with respect to steam in comparison to hydrocarbons indicated the dissociation of steam: this was consistent with the results observed by kinetic of isooctane steam reforming. As a result, it was justified to fit the data in to the Langmuir-Hinshelwood (LH) Model 3 of the isooctane steam reforming. Table 8.11 shows the results.

Table 8.11 Estimates of LH model 3

Temp. (°C)	k_{rxn}	K_A	K_B	SSE
375	0.0020	4338.8	284.1	10.9
400	0.0027	3070.4	171.1	29.5
425	0.0037	1806.1	103.1	441.3

A : effective hydrocarbons; B : steam.

The sum of squares of errors were bigger than the results obtained for individual steam reforming of isooctane probably due to the simplification introduced in the estimation of the partial pressures of components in the artificial gasoline. Interestingly, the activation energy obtained by model 3 (Table 8.12) was almost the same as the value obtained from the isooctane kinetics. Indeed, the estimates of this model also satisfied BMV criteria as shown by Table 8.13.

Table 8.12 Estimate of activation energy for model 3

$1/T, \text{K}^{-1}$	$\text{Ln } k_{\text{rxn}}$	$E, \text{kJ mol}^{-1}$	R^2
0.00154	-6.19	-44.9 ± 4.2	0.991
0.00149	-5.93		
0.00143	-5.59		

Table 8.13 Estimates of model 3 for BMV guidelines

Parameter	Corr. Coeff. (r^2)	$-\Delta S > 10$	$-\Delta S < (12.2 - 0.0014 \Delta H)$
$\Delta H_A, \text{J mol}^{-1}, -65717$	0.980		
$\Delta S_A, \text{J mol}^{-1} \text{K}^{-1}, -31.5$	0.980	$31.5 > 10$	$31.5 < 104.2$
$\Delta H_B, \text{J mol}^{-1}, -76250$	0.999		
$\Delta S_B, \text{J mol}^{-1} \text{K}^{-1}, -70.6$	0.999	$70.6 > 10$	$70.6 < 118.9$

Figure 8.12 compares the observed rate versus the predicted rate based on the power law and LH expression in model 3.

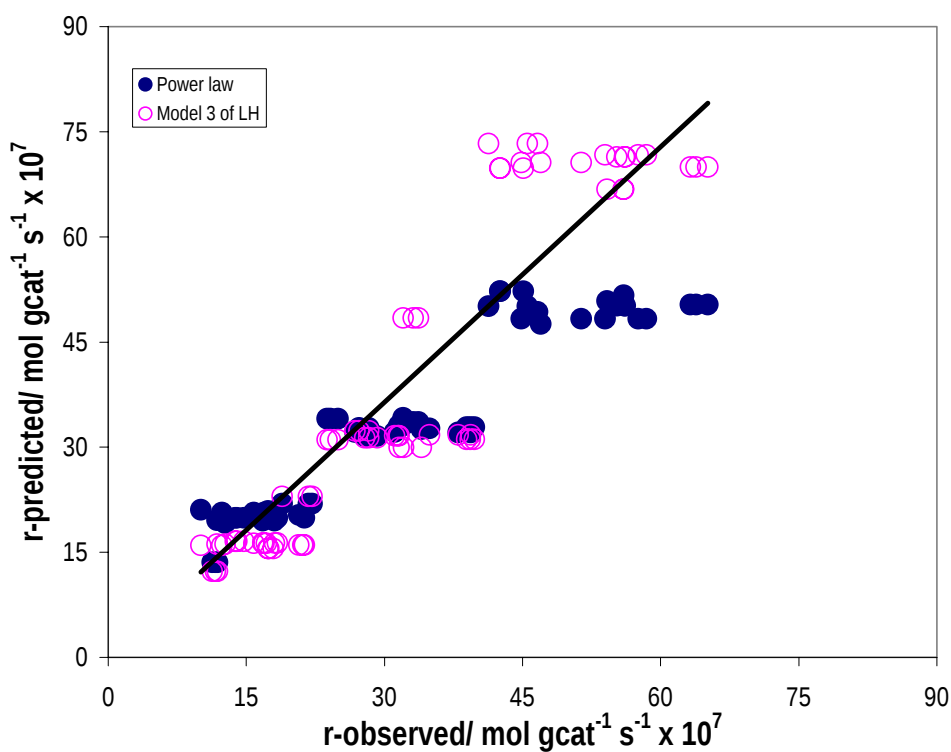


Figure 8.12 Observed rate versus predicted rate for the steam reforming of artificial gasoline.

From Figure 8.12, it is apparent that LH model 3 predicted higher rates than the power law model only at the highest reaction temperatures used. No attempts were made to fit the

kinetic data to models 1,2,4,5, and 6, since previous assessments with isooctane data were unsuccessful.

8.5 Conclusions

Kinetic studies of the steam reforming of isooctane were carried out over a nickel-based catalyst at atmospheric pressure and at different temperatures. A power law rate of the form:

$$(-r) = 0.0026 \exp^{\frac{-44,000 \frac{\text{J}}{\text{mol}}}{RT}} p_{\text{C}_8\text{H}_{18}}^{0.17} p_{\text{H}_2\text{O}}^{0.54}$$

described the data. Fitting the experimental data to the Langmuir-Hinshelwood expression shows that the rate determining step in the steam reforming of isooctane involves the reaction between dissociatively adsorbed species of isooctane and steam. The resulting activation energy is comparable to the steam reforming of other hydrocarbons.

Similar studies were also carried out for artificial gasoline and a power law rate of the form :

$$(-r) = 0.291 \exp^{\frac{-66,800 \frac{\text{J}}{\text{mol}}}{RT}} p_{\text{he}}^{0.08} p_{\text{s}}^{0.23}$$

fitted the data .

The derived kinetic expressions may be used to predict fuel consumption rate from a compact autothermal fuel processor.

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Chapter 9 Autothermal reforming of artificial gasoline at ambient temperature

9.1 Introduction

Studies of partial oxidation (Chapter 6) and steam reforming of gasoline-like hydrocarbons (Chapter 7) have indicated that the overall oxidation/reforming system offers an efficient route for the production of hydrogen. The autothermal reforming of methane [1, 2], methanol [3, 4], and light hydrocarbons [5] have been successfully demonstrated.

The feasibility of autothermal reforming (ATR) of isooctane as a model for gasoline at ambient temperature was investigated. The study involved raising the catalyst bed temperature to a value such that the oxidation of isooctane to produce heat and steam occurred. This was done either by combusting an initiator such as hydrogen, to effect the auto-ignition of the mixture of isooctane and oxygen at a specified ratio, or by using an electrically powered furnace. The heat evolved increased the catalyst bed temperature to at least a value such that the steam reforming of unburnt isooctane to produce hydrogen occurred.

The oxidation of isooctane is expected to approach completion sooner than that of steam reforming, and thus the effect of total oxidation should be considered in terms of a predetermined degree of conversion [6, 7]. It was observed from the studies of isooctane

oxidation that, by the use of an oxygen to carbon ratio of ca. 1 to 1.5, about 30 to 50% of isooctane feed could be combusted to carbon dioxide and water (Chapter 6), but the water produced was not sufficient for the steam reforming of the remaining isooctane. As a result, additional water must be injected at the inlet of the reactor. Since a steam to carbon ratio of ca. 3 in the reaction system is required to minimise coke formation on Ni catalyst, and the amount of remaining unburnt isooctane can be predicted from the oxidation reaction, the minimum amount of additional water required can be estimated.

There is no doubt that heat and mass transfer within the system (supplying heat and steam from isooctane oxidation and consuming heat and steam for hydrocarbon reforming), are of prime importance.

9.2 Experimental methods

9.2.1 Catalysts

Previous studies for the autothermal reforming (ATR) of light hydrocarbons revealed that a bi-functional catalyst of Pt-Ni/ δ -Al₂O₃ was the most efficient system for hydrogen production by both oxidation and steam reforming in comparison to either a dual-bed of Pt/ δ -Al₂O₃ and commercial nickel-based catalyst (Ni-com), or a single bed of physically mixed Pt/ δ -Al₂O₃ and

Ni-com [5]. As a result, a Pt/Ni-com catalyst, prepared in the laboratory by the techniques described in Chapter 4 was tested.

A Pt/CeO₂ catalyst was also tested, since Pt/CeO₂ and Pd/CeO₂ have been successfully employed for the steam reforming of higher hydrocarbons [8-10]. The catalyst preparation techniques were reported in Chapter 4.

Under normal circumstances, all catalyst fine powders were pelletised, ground and sieved to 300 – 425 microns. Dusty particles of less than 200 microns were unavoidable when the pelletising machine was out of order. The physical properties of the catalysts used are listed in Table 9.1.

Table 9.1 Physical properties of the catalysts used

Properties	Pt/CeO ₂	Ni-com	Pt/Ni-com
Metal content, %	2 – 3 as Pt	34 as NiO	2 – 3 as Pt/34 as NiO
BET surface area, m ² g ⁻¹	26.4±0.3	11.0±0.2	9.9±0.8
Pore size diameter (BJH desorption), nm	7.6	21.2	17.5
Bulk density, g mL ⁻¹	0.43±0.01	1.12±0.01	1.11±0.004

Both unreduced and in-situ reduced samples (reduced at 600 °C for four hours using a 20 % hydrogen in nitrogen) were investigated. Details of the reduction conditions were described in Chapter 3.

A composite metal catalyst (Pt/Ni-com) and a Pt/CeO₂ catalyst were employed for the autothermal reforming (ATR) of isooctane. All experiments were undertaken in a single tubular stainless steel reactor of 10 mm ID as mentioned in Chapter 3. About 0.1 g of catalyst diluted in 0.9 g of α -Al₂O₃ was loaded into the reactor. Table 9.2 provides a summary of the process conditions.

Table 9.2 Process conditions used for autothermal reforming of isooctane

Description	Values
Water bath temperature, °C	51
i-Octane/N ₂ , mL min ⁻¹	80
O ₂ , mL min ⁻¹	60
Water flow, mL h ⁻¹	3
Water evaporator temperature, °C	200
Catalyst loading (either Pt/Ni-com or Pt/CeO ₂), g	0.1

9.2.2 Catalyst testing with isooctane

In starting-up the system, three different techniques were adopted. The first used a two-step mixture of H₂ and simulated air (H₂ : O₂ : N₂ = 62.7 % : 8.3 % : 28 % for the first step and 38.1 % : 12 % : 49.9 % for the second step). The amount of hydrogen and oxygen required as initiators was estimated based on previous studies [1]. The simulated air, consisted of separate metered pure O₂ and N₂.

Secondly, a new technique involving auto-ignition of the mixture of hydrocarbon, oxygen, and nitrogen was employed. No hydrogen or electrical heating was required to initiate reaction.

The last step of reaction initiation involved heating the catalyst bed electrically while feeding the reactants into the reactor. Once the hydrocarbon lit off, the electric power was switched-off and self-sustained ATR was attained.

The catalyst bed and furnace temperatures were monitored individually by two independent thermocouples, while both temperatures were recorded manually. Isooctane was picked-up from a saturator by introducing N_2 into the saturator at a certain flow rate. The saturator temperature was controlled by immersing a Dreschel bottle in a Julabo thermostated water bath. There were two Dreschel bottles; the first bottle was filled with packing materials consisting of glass beads, Raschig rings, spiral rings, and hydrocarbon. The ratio of loaded packing materials, hydrocarbon, and vapour chamber was ca. 1 : 1 : 1 (measured as fraction of height of the bottle) to ensure a maximum hydrocarbon pick-up capacity at a specified temperature. The second bottle was loaded with similar packing materials, since this saturator was dedicated to stabilise the amount of hydrocarbon picked-up. All gaseous feeds were metered individually by Brooks 5850E mass flow controllers using independent lines to ensure the flexibility of manipulating feed compositions.

Water was pumped into the evaporator by a micro-computer controlled ISCO syringe pump 260 D. The inlet and by-pass lines to and from reactor were wrapped with heating tape to

avoid condensation. When the auto-ignition experiments were attempted, the evaporator was by-passed and the heating tapes were turned-off to ensure attainment of true auto-ignition.

It was necessary to remove water from the product stream before analysis of gases. When the inlet concentration of hydrocarbon was high (inlet bath temperature = 51 °C), excess water in the products was removed using a glass condenser and a Drierite (calcium sulphate filled 150 mm long and 10 mm I.D. quartz tube) moisture trap operated at room temperature. When the inlet concentration was low (bath temperature 20 – 25 °C), the glass condenser was immersed in the water bath whilst the Drierite moisture trap was kept at room temperature. The inlet or outlet reactor flow rates measurement was checked using a bubble meter. In this case, the Drierite tube was by passed and uncondensed water was trapped in the second condenser immersed in a bucket filled with a mixture of ice cubes and tap water. Figure 3.2 (Chapter 3) provides a simplified diagram of the experimental rig.

9.2.3 Catalyst testing with artificial gasoline

It is intended to mix 8.3 % of cyclohexane, 58.4 % of isooctane and 33.3 % of octane on a volume basis as a formula for the artificial gasoline (Chapter 7).

A three-saturator feeding system was required. The first saturator was filled with a mixture of 25 mL cyclohexane (boiling point ca. 81 °C) and 175 mL isooctane (boiling point ca. 99 °C), whilst the second saturator was filled with 100 mL octane (boiling point ca. 125 °C). The third saturator was used as a stabiliser pot. Packing arrangement inside the saturators was

described in Chapter 3. The Julabo-E thermostat was controlled at 75 °C. Additional heating tape (controlled at 75 °C) was wrapped along the teflon tubes leading to the inlet of all gas chromatographs. Due to the lower purity of octane used (98 %) in comparison to the previous artificial gasoline composition (at least 99 % for all hydrocarbons), a small amount of toluene was detected (ca. < 1%).

The initial experiments with artificial gasoline used the same approach as with isooctane, first oxidising and then steam reforming the fuel (Figure 9.2). Since a vehicle mounted catalyst would have to survive many stop-start operations, several cycles of experiments were carried out. These can be conveniently summarised using the graphs (Figures 9.6 – 9.16).

Initial start-up involved admitting 291 mL min⁻¹ nitrogen split in equal amounts into two hydrocarbon filled saturators and passed over the catalyst bed for 1-2 min. An oxygen flow of 86 mL min⁻¹ was then added into the system. Table 9.3 provides a summary of the process conditions.

Table 9.3 Process conditions used for autothermal reforming of artificial gasoline

Description	Values
Water bath temperature, °C	75
Hydrocarbons/N ₂ , mL min ⁻¹	291
O ₂ , mL min ⁻¹	86
Water flow, mL h ⁻¹	14.6
Water evaporator temperature, °C	200
Catalyst loading, g	
• Pt/CeO ₂	0.2
• Ni-com	0.3

9.3 Results and discussions

9.3.1 Autothermal reforming of isooctane over Pt/Ni-com catalysts

The catalyst bed was reduced as described in Chapter 3. A mixture of hydrogen, oxygen, and nitrogen were fed at room temperature through the catalyst bed as an initiator to achieving bed temperatures up to ca. 370 °C, as depicted by Figure 9.1. The lower part of this curve indicated a significant loss of heat by convection, even though the gap between reactor wall and the furnace wall was filled with alumina as an insulating material. From initial experiments, there was no significant difference in the hydrogen combustion profile for this particular catalyst, regardless of the catalyst's reduction state. This experiment demonstrated that the initiation of reaction by a mixture of hydrogen and air [1] was reproducible. However, care should be taken in using hydrogen/air mixture due to the explosive limits.

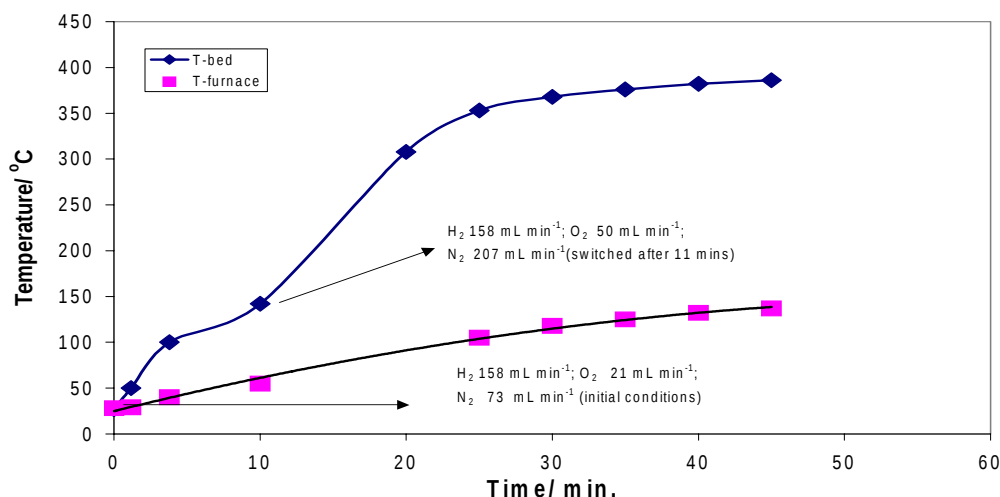


Figure 9.1 A two-step hydrogen combustion

The catalyst was then re-reduced by similar methods in order to reactivate any oxidised catalyst and then was cooled to ambient temperature under flowing 20 % hydrogen in nitrogen. A mixture of isooctane in nitrogen was then passed over the catalyst for about 1-2 min and, subsequently, oxygen was also fed into the reactor to give a total flow rate of ca. 140 mL min⁻¹ (O:C = 1.6). As depicted by Figure 9.2, the catalyst bed temperature rose rapidly and attained a steady state value of ca. 380 °C. Isooctane converted was ca. 50 %. No hydrogen was detected, indicating that partial oxidation was not significant. Initially, saturator temperatures of 20 and 25 °C were used, but, the amount of isooctane picked-up was not sufficient to provide the required heat for ATR. To attain a self-sustaining autothermal reforming, a minimum isooctane concentration of ca. 5 % was required.

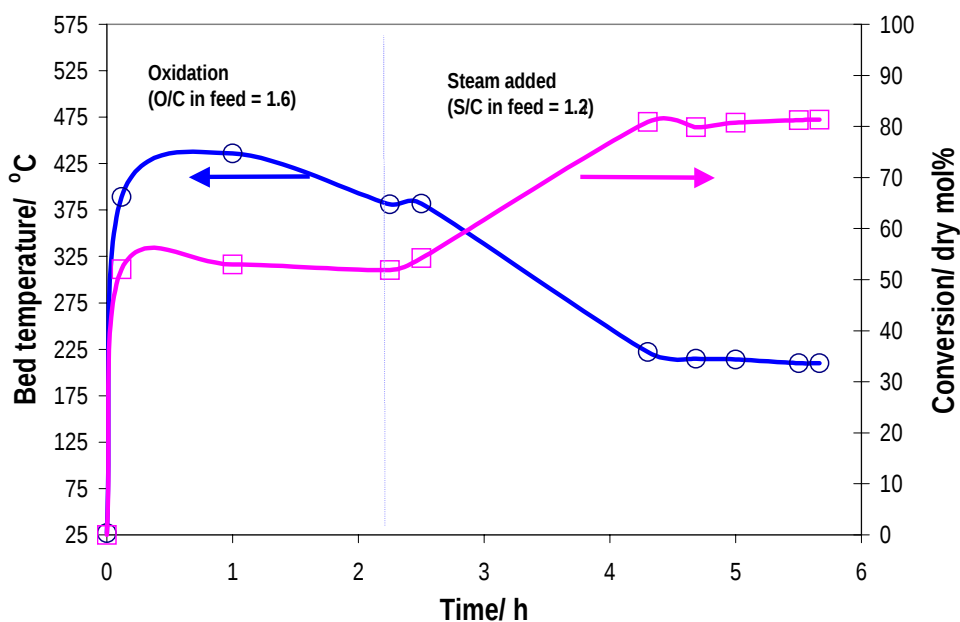


Figure 9.2 Catalyst bed temperature and isooctane conversion (Total dry gas 141 mL min⁻¹; water 3 mL h⁻¹; Pt/Ni-com catalyst loaded 0.1g)

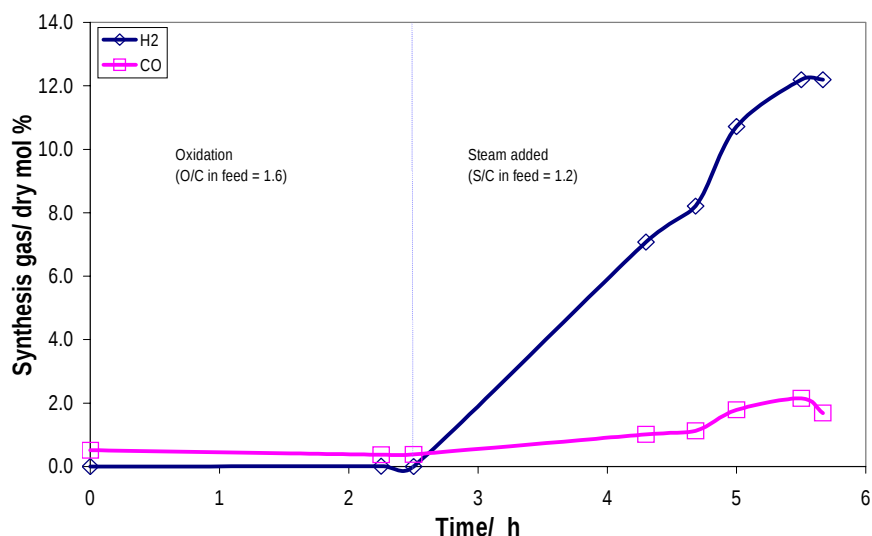


Figure 9.3 Synthesis gas product distribution (Total dry gas 141 mL min⁻¹; water 3 mL h⁻¹; Pt/Ni-com catalyst loaded 0.1g; O:C = 1.6:1)

The amount of fuel combusted was then calculated and sufficient water added to provide a steam:carbon (S:C) ratio of 1.2:1 based on the residual isooctane. A water flow of ca. 3 mL h⁻¹ was evaporated at 200 °C in a pre-heater. The reaction temperature dropped to ca. 215 °C (Figure 9.2) due to steam reforming. Synthesis gas production attained steady state after above 5 hours of operation. A significant amount of hydrogen (ca. 12 %) and ca. 2 % of CO were produced as shown by Figure 9.3 (H₂ : CO ratio = 6 : 1) and the isooctane conversion rose to ca. 80 % (Figure 9.2). The increased ratio above the value expected from reaction (5.3) was probably due to coke formation from CO.

When the sequence of start up was changed i.e. by introducing oxygen first followed by adding isooctane/nitrogen, the catalyst was totally deactivated. This was not surprising since the

active sites were covered by adsorbed oxygen, and the catalyst was oxidised prior to commencing the reaction with isooctane.

9.3.2 Autothermal reforming of isooctane over Pt/CeO₂ catalysts

The autothermal reforming of isooctane was also undertaken over a Pt/CeO₂ catalyst. The pre-treatment of catalyst sample as well as the start up techniques was exactly the same as those employed in the previous experiment.

As seen in Figure 9.4, total conversion of isooctane was about 90 % or 10% higher than that obtained over Pt/Ni-com catalyst. This was due to the fact that the concentration of isooctane in the feed was slightly less than that used in the Pt/Ni-com run. As a result, for the same amount of oxygen and nitrogen diluent, the oxygen to carbon and steam to carbon ratios increased. Thus, it was not surprising that no significant difference in conversion was observed either before or after steam injection.

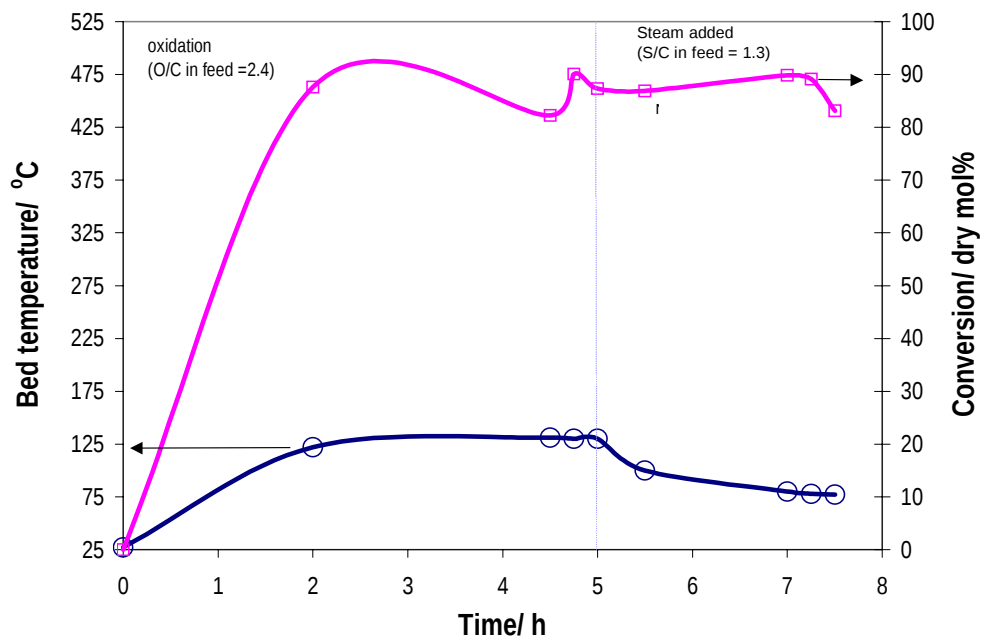


Figure 9.4 Catalyst bed temperature and isooctane conversion (Total dry gas 139 mL min⁻¹; water 3 mL h⁻¹; Pt/CeO₂ catalyst loaded 0.1g)

In contrast to Figure 9.2, the recorded bed temperature was very low for the attainment of such a high conversion, possibly due to incorrect positioning of the inserted thermocouple in the catalyst bed. Examination of Figure 9.3 and Figure 9.5 revealed that there was no significant difference in the production of hydrogen.

In conclusion, these two preliminary experiments proved that the autothermal reforming of isooctane may be conducted at ambient temperature, provided that the catalyst was pre-reduced and the appropriate sequence of start-up was followed.

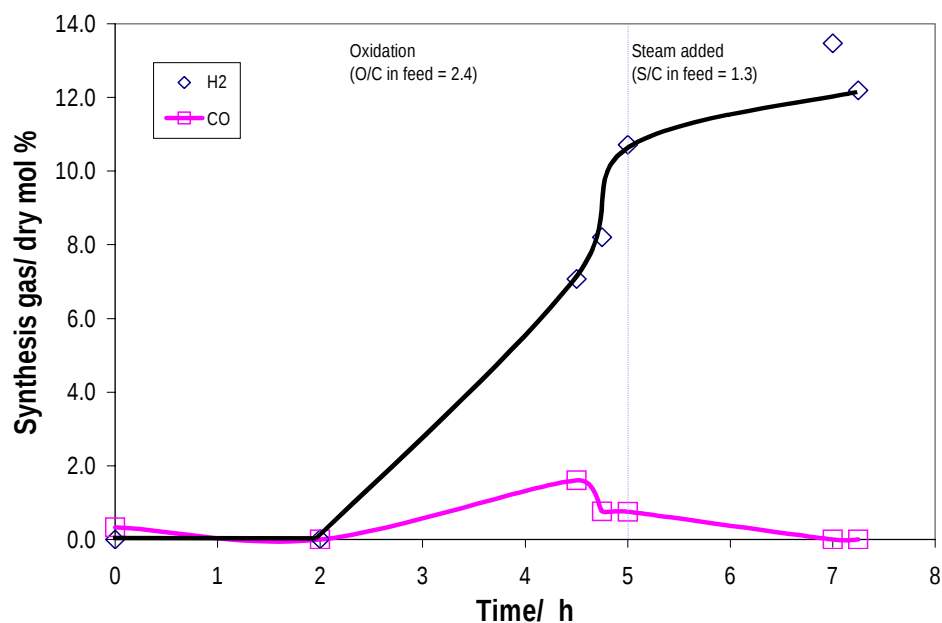


Figure 9.5 Synthesis gas product distribution (Total dry gas 139 mL min⁻¹; water 3 mL h⁻¹; Pt/CeO₂ catalyst loaded 0.1g).

9.3.3 Autothermal reforming of artificial gasoline

9.3.3.1 The approach to steady state

As described in Section 6.1, it was intended to carry out the autothermal reforming of a higher hydrocarbon mixture over a dual bed catalyst. Part of the fuel should be combusted to generate heat, which is required for the steam reforming operation.

The amount of fuels to be burned was estimated by simple material and heat balances based on the result of ATR of isooctane over Pt/Ni-com (Section 9.3.2). The calculation is reported in Appendix VI. The results show that ca. 0.02 mol h⁻¹ hydrocarbon feed equivalent to isooctane has to be combusted in order to raise catalyst bed temperature above 500 °C.

Both Pt/CeO₂ (0.2 g) and Ni-com (0.3 g) catalysts were then loaded separately in a single tubular reactor. The platinum based catalyst was packed in the reactor upstream of the Ni-com catalyst, separated by quartz wool ca. 5 mm thick. All catalysts were reduced at 600 °C by 20 % hydrogen in nitrogen for four hours.

In the first cycle, a mixture of artificial gasoline, nitrogen and oxygen was just admitted to the reduced catalysts.

The furnace was heated to 250 °C at 5 °C min⁻¹ while the bed temperature was carefully monitored. When the bed temperature reached ca. 180 °C, a dramatic temperature excursion up to ca. 580 °C was observed and the furnace was quickly turned-off. Figures 9.6 and 9.7 display the observed results.

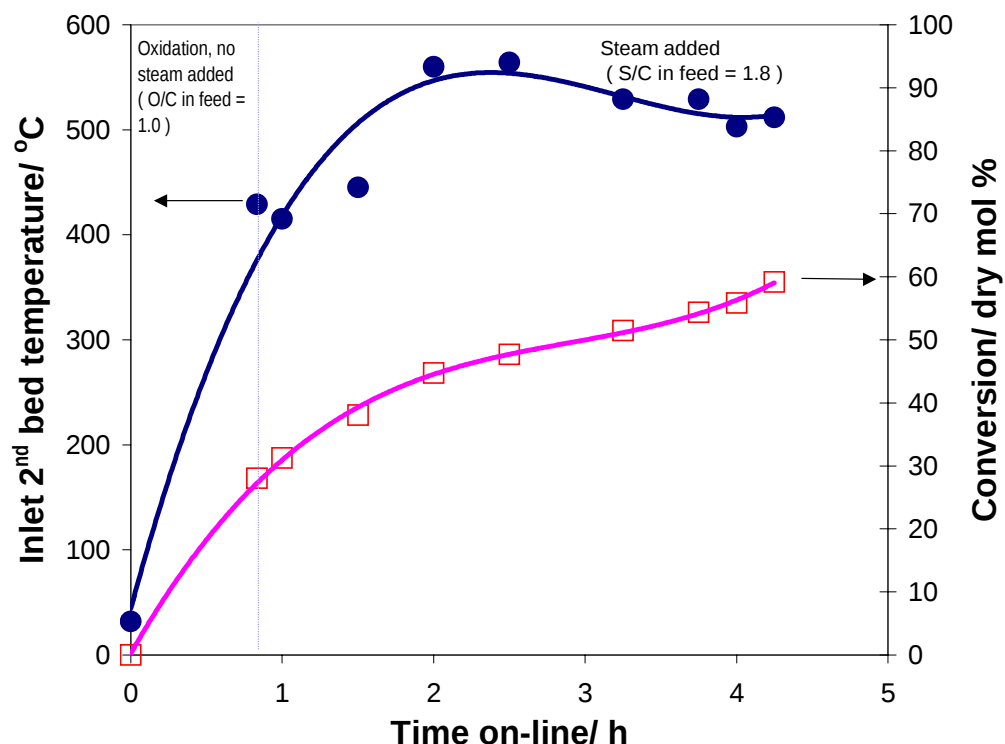


Figure 9.6 Catalyst bed temperature and artificial gasoline conversion from the first cycle (total dry gas flow = 377 mL min⁻¹; two bed system with total catalyst loaded = 0.5 g)

As predicted from previous light off experiments for the artificial gasoline (Chapter 6), about 30 % of the inlet hydrocarbons were combusted when an O:C ratio of 1 was supplied. About 14.6 mL min⁻¹ of water (S:C = 1.8:1) was then evaporated at 200 °C in the pre-heater and subsequently admitted to the reactor. An unexpected temperature rise at the catalyst bed was observed (Figure 9.6), probably due to the oxidation of part of pre-reduced catalyst. Conversion increased to ca. 55 % when steam was introduced. Steady state was attained after 4 hours of operation.

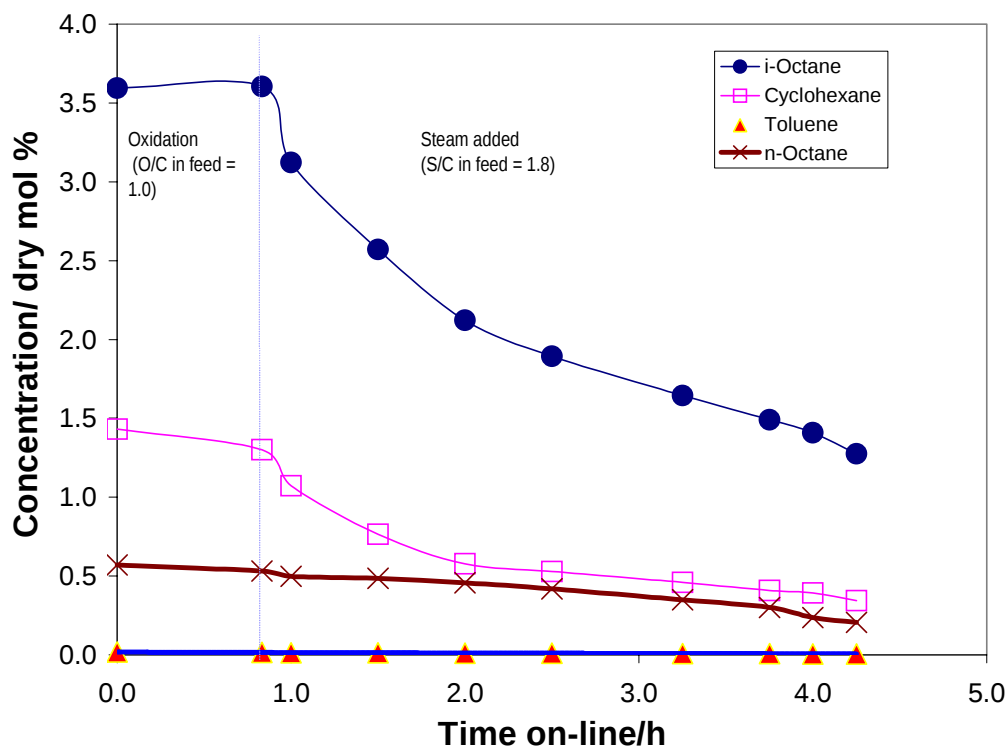


Figure 9.7 Concentration profile for the autothermal reforming of artificial gasoline from the first cycle (total dry gas flow = 377 mL min⁻¹; two bed system with total catalyst loaded = 0.5 g)

As seen in Figure 9.7, all hydrocarbons were consumed at almost the same rate. Examination of Figure 9.8 shows that very little hydrogen was produced during the oxidation regime and this may have come from steam reforming of hydrocarbons involving the small amount of steam generated by combustion. Hydrogen was produced significantly only when oxygen was used up (Figure 9.8) and additional steam was admitted to the system. It was interesting that, whilst only a few ppm of ethylene and butene were produced during the oxidation of hydrocarbons, the amount of ethylene produced during steam reforming increased quite significantly, probably due to the increased steam catalytic cracking of hydrocarbons [11]. This was consistent with the results observed for the steam reforming of artificial gasoline (Chapter 7).

Carbon dioxide increased slightly on addition of water, whilst only a small amount of methane was observed. It was not surprising that carbon monoxide was not detected as the WGS reaction would produce carbon dioxide at the reaction temperature observed.

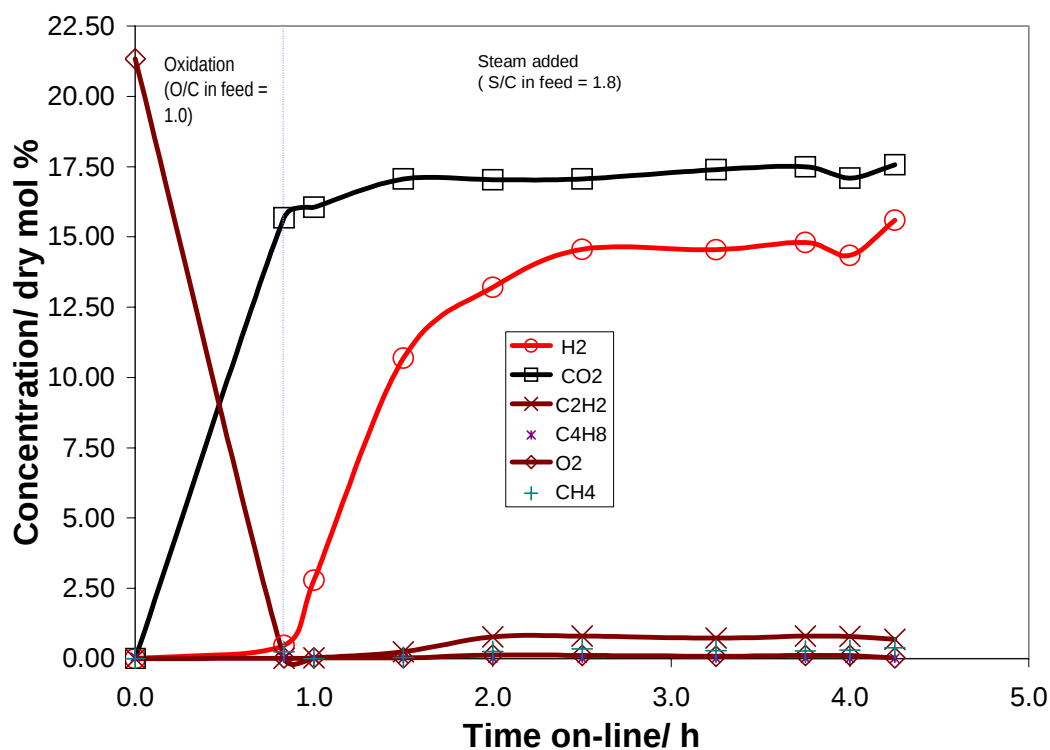


Figure 9.8 Product distribution for the autothermal reforming of artificial gasoline from the first cycle (total dry gas flow = 377 mL min⁻¹; two bed system with total catalyst loaded = 0.5 g)

Since the auto-ignition of the mixture of isooctane and oxygen at ambient temperature was feasible (Section 9.3.1), a similar result was also expected for the artificial gasoline system.

The catalyst was oxidised under ca. 70 mL min⁻¹ of 3 % oxygen in nitrogen at 600 °C for 4 hours in order to burn-out any carbonaceous material. The bed was then cooled to ambient, and 100 mL min⁻¹ of 20% hydrogen in nitrogen was admitted to the reactor. The catalyst was then re-reduced by previously used methods (Chapter 3).

From the light off experiments involving the hydrocarbon mixture (Section 6.3.5), the extent of oxidation involved competitive adsorption among the individual components and oxygen molecules on catalyst active sites. As a result, the start-up sequence was modified.

In the second cycle, a mixture of hydrocarbons, oxygen and nitrogen diluent was admitted simultaneously over the reduced catalyst at ambient temperature. As expected, the bed temperature rose dramatically within 5 minutes. The analysis of the outlet reactor composition was taken several times, shortly after 8 minutes of operation and subsequently at intervals of ca. 12 minutes. At about the 45th minute, steam (equivalent to 23.8 mL min⁻¹ of water flow rate) was injected over the reactor (S:C = 3.4:1). In the context of hydrogen production on-board a vehicle, a high S:C ratio is not desirable due to increased weight of water in the vehicle: however, the risk of carbon formation, especially during transient operation, must be minimised.

9.3.3.2 Steady state

As a compromise, the amount of water injection was reduced to 14.6 mL min⁻¹ after steady state condition was attained, in order to obtain a steam to carbon ratio of ca. 2 in the feed.

Even though simulation studies of ATR for isooctane [6] showed that the hydrogen yield was highest at water : octane ratio of 11.4 (S:C ~ 1.4), the ratio of steam to carbon was kept at ca. 2 in order to minimise the risk of carbon formation. Figures 9.9 to 9.12 display the observed results.

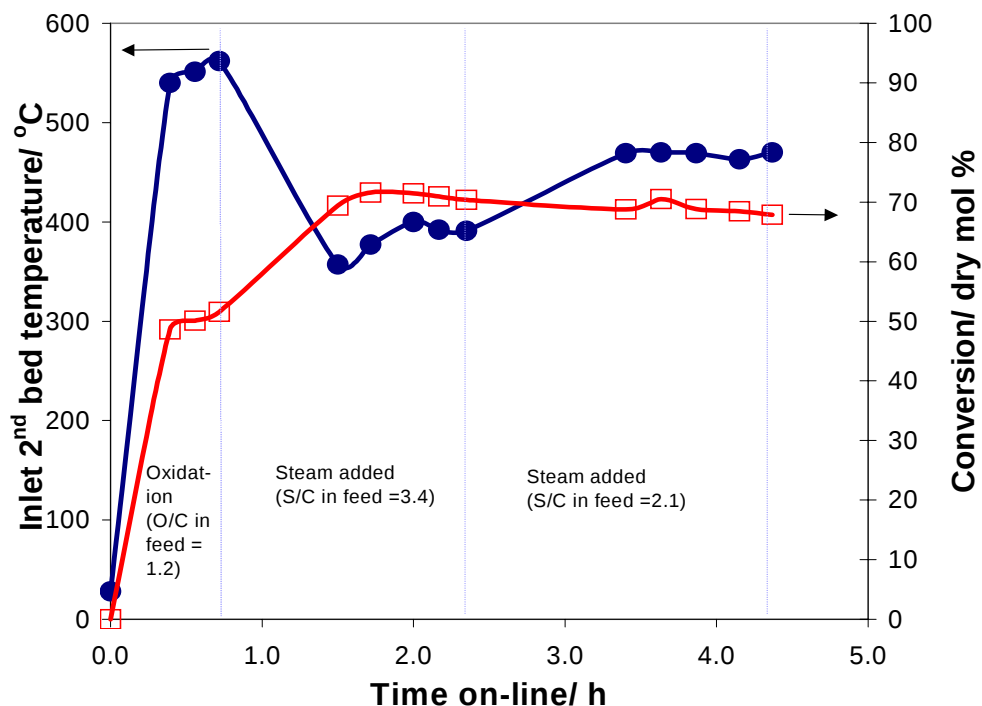


Figure 9.9 Catalyst bed temperature and artificial gasoline conversion from the second cycle (total dry gas flow = 377 mL min⁻¹; two bed system with total catalyst loaded = 0.5 g)

In comparison to Figure 9.6, by slightly increasing O:C ratio in the feed, about 50 % of inlet hydrocarbons was combusted (Figure 9.9). This was in agreement with the previous light off experiments (Chapter 6). The maximum bed temperature was about 584 °C or ca. 20 °C higher than that of the inlet second bed temperature.

As expected, when steam was added the bed temperature dropped. Some heat was removed due to the need to increase steam temperature from ca. 200 °C to the steady state reaction temperature. Some heat was removed due to heat utilised for steam reforming of hydrocarbons. By using the net heating value for the combustion of isooctane of

ca. $-5100 \text{ kJ mol}^{-1}$ [6], the amount of heat evolved resulting from the combustion of 50 % of hydrocarbons was ca. 2700 kJ h^{-1} . The heat absorbed by $1.32 \text{ moles h}^{-1}$ of steam in order to increase temperature from $200 \text{ }^{\circ}\text{C}$ to ca. $400 \text{ }^{\circ}\text{C}$ was about $7.8 \text{ kJ mol}^{-1} \times 1.32 \text{ moles h}^{-1}$ or ca. 10 kJ h^{-1} (or only ca. 0.4 % of the liberated heat from hydrocarbons combustion). Thus, besides heat loss to the surrounding, most energy produced was used for steam reforming in order to increase the conversion from 50 % to ca. 70 %. Decreasing the amount of steam from $1.32 \text{ moles h}^{-1}$ (S:C=3.4:1) to $0.81 \text{ moles h}^{-1}$ (S:C=2.1:1), only decreased the conversion by ca. 2 %.

Table 9.4 displays the observed results and the results based on the simulated autothermal reforming of octane using Gibbs free energy minimisation methods (Chapter 5), and employing the same process conditions applied to the experimental autothermal reforming of artificial gasoline.

To boost the overall conversion to 100 %, more hydrocarbons and more oxygen should be fed to the reactor. Unfortunately, it was not possible to increase the saturator temperature to more than $75 \text{ }^{\circ}\text{C}$ due to the cyclohexane boiling point ($81 - 82 \text{ }^{\circ}\text{C}$). As a result, no further optimisation studies were attempted.

Examination of Figure 9.10 revealed that isooctane and octane were significantly oxidised whilst cyclohexane was less oxidised. This was unexpected, based on the previous light off runs for mixed hydrocarbons as well as from the first cycle results (Figure 9.7). Repeating the oxidation run only after the completion of an autothermal run for a prolonged period (results

reported below in Figure 9.15) showed that cyclohexane was also significantly oxidised. It was therefore suggested that the peculiarity of cyclohexane oxidation behaviour as shown by Figure 9.10 was induced by the variation of cyclohexane concentration during transient operation.

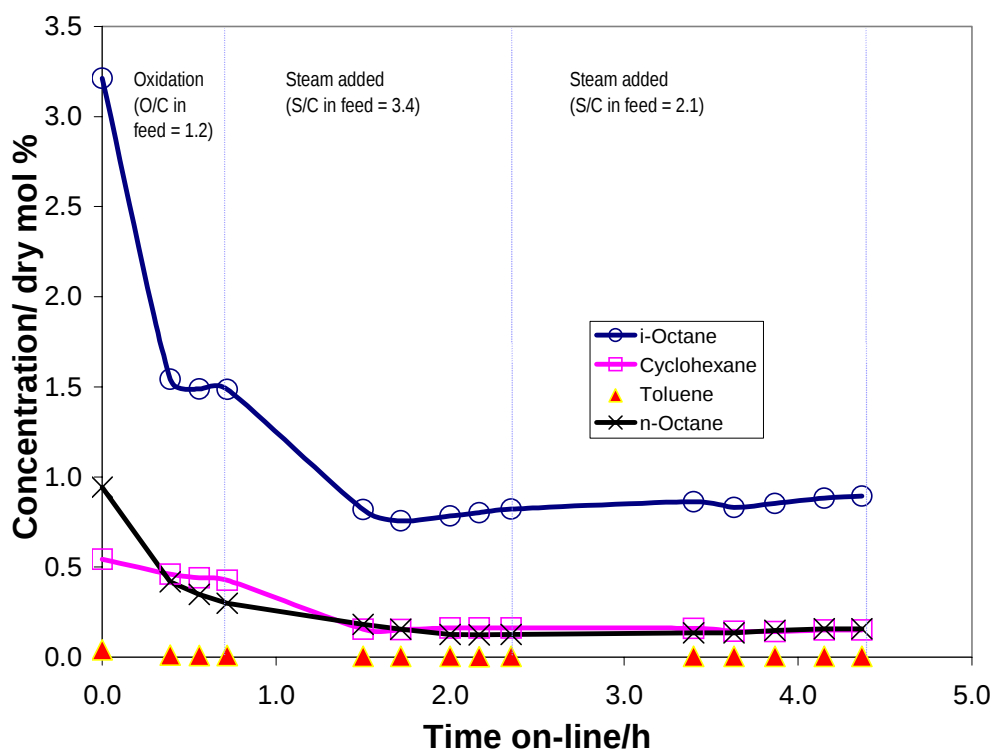


Figure 9.10 Concentration profile for the auto thermal reforming of artificial gasoline from the second cycle (total dry gas flow = 377 mL min⁻¹; two bed system with total catalyst loaded = 0.5 g)

The individual hydrocarbons conversion profile in the steam reforming regime was as expected, and comparable to the results observed for the steam reforming of mixed hydrocarbons (Chapter 7).

Figure 9.11 shows the product distribution for the entire operation of the second cycle. The amount of hydrogen produced increased by about 2.5 times after complete depletion of oxygen and first addition of extra water (amounting to a S:C of 3.4). This would indicate that more hydrogen was produced by steam reforming of unburnt hydrocarbons.

The maximum conversion for the combustion reaction was then limited to ca. 50% and no further optimisation studies were attempted. Decreasing the injected steam by 40 % decreased the hydrogen produced by ca. 1-2 % only, and this condition was maintained at ca. 2 hours without sign of catalyst deactivation. This suggested that the S:C of 2.1 could be considered as the optimum value. The occurrence of acetylene and butene (Figure 9.11) was probably due to the catalytic cracking of hydrocarbons which was enhanced by the higher S:C ratio. This was consistent with the results of the first cycle. Whilst about 16 % of CO₂ was produced, about 1.3 % carbon monoxide was produced by oxidation and, when the S:C ratio was maintained at 3.4, the carbon monoxide level decreased to ca. 0.5 %. When the S:C ratio was reduced to 2.1, the carbon monoxide quantity increased to ca. 0.8%. This would suggest that the water gas shift reaction (WGS) played an important role and that the WGS was enhanced by higher steam concentrations.

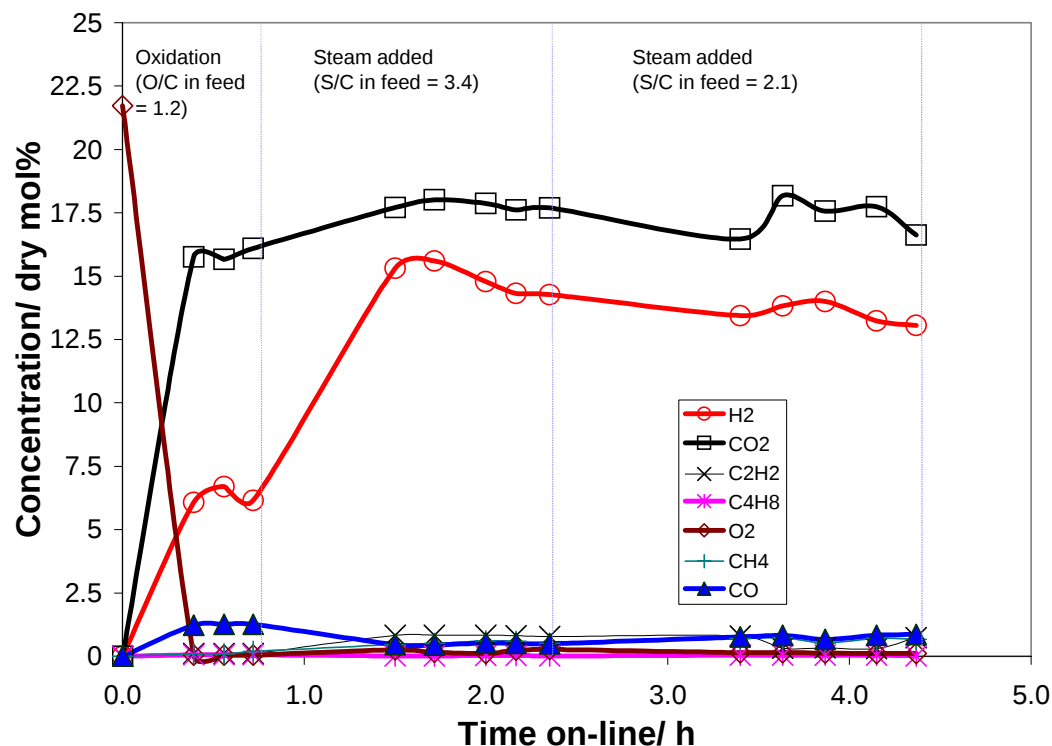


Figure 9.11 Product distribution for the auto thermal reforming of artificial gasoline from the second cycle (total dry gas flow = 377 mL min⁻¹; two bed system with total catalyst loaded = 0.5 g)

Further examination of product yields as presented by Runs 2 and 3 (Table 9.4) revealed that the extent of methane steam reforming and the WGS reaction was enhanced by increasing amount of injected steam and this was as expected [12].

Table 9.4 Results observed and simulated from the autothermal reforming of artificial gasoline

RUN	1	2	3
Feedstock			
O : C	1.2	1.2	1.2
S : C	0	3.4	2.1
GHSV ^a , h ⁻¹	27000	60800	47700
T ₁ ^b , °C	562	391	470
T ₂ ^c , °C	584	n/a (768)	566 (515)
T _{average} , °C	573	n/a	518
Conversion, mol%	51.6	70.3 (100)	67.9 (100)
RHPE ^d (%)	n/a	26.9	33.1
Product yield, (mol/atom carbon fed) x 100%			
H ₂	16.6	44.0(162.8)	39.1(118.2)
CO ₂	43.5	54.5(68.2)	49.8(17.4)
CO	3.4	1.5(31.8)	2.6(11.0)
CH ₄	0.5	1.6(0.01)	2.0(15.4)
C ₂ H ₂	0.3	2.4 (0)	2.2 (0)
C ₄ H ₈	0.2	0.1 (0)	0.1 (0)
H ₂ , mol% in dry gas	6.1	14.3 (35.2)	13.1 (28.3)
H ₂ selectivity, (mol H ₂ /atom carbon consumed)x100%	34.2	70.1(162.8)	66.3(118.2)
Notes : ^a based on total volume of both catalysts ^b inlet 2 nd bed ^c outlet 2 nd bed ^d RHPE : $\frac{(\text{observed value of hydrogen produced}) \times 100\%}{(\text{calculated hydrogen based on thermodynamics})}$ n/a not available; () simulated values			

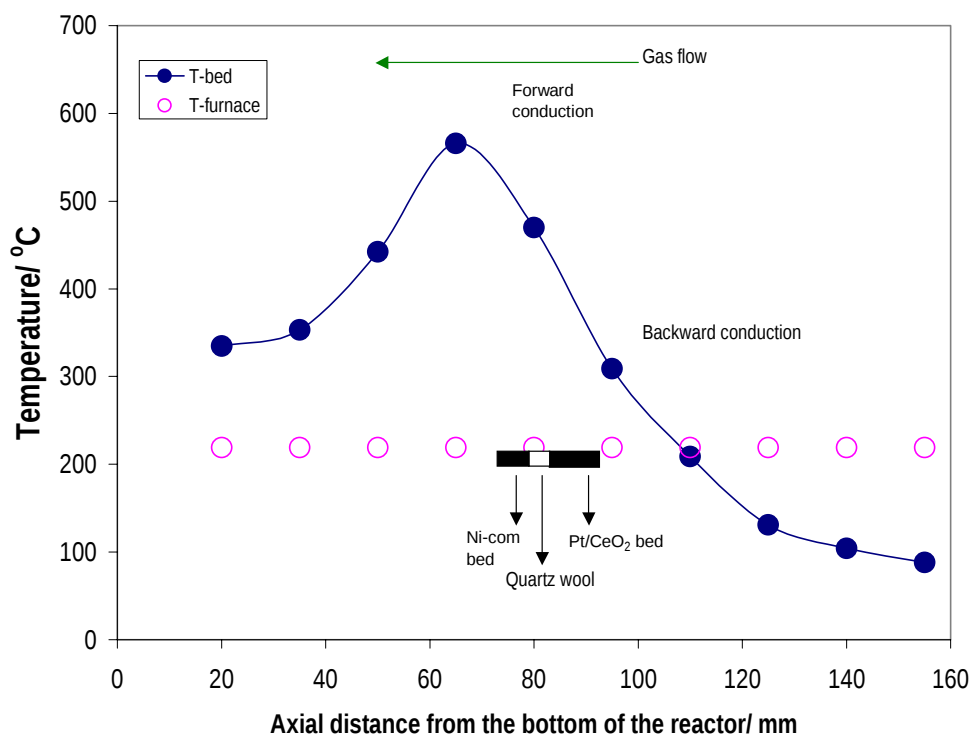


Figure 9.12 Axial temperature distribution during the auto thermal reforming of artificial gasoline from the second cycle at the optimum steam/carbon ratio of 2.1 (total dry gas flow 377 mL min^{-1} ; two bed system with total catalyst loaded = 0.5 g).

9.3.3.3 Temperature profiles

Figure 9.12 shows the temperature profile of the catalyst bed as measured during the ATR operation at the optimum S:C ratio of 2.1. The inlet temperatures of the first and second bed were found to be lower than that of the outlet temperature of the second bed. This was caused by backward conduction of heat towards the front of the reactor and forward conduction brought about by transfer of heat involving the hot gases, the material of the reactor and the thermowell. All temperature measurements were repeated and were within $\pm 2 \text{ }^{\circ}\text{C}$.

The measured furnace temperature was ca. 200 °C, which indicated a significant heat loss from the reactor wall to the surrounding (alumina insulator was placed between outer reactor wall and inner furnace wall).

If the reactor is assumed to be a heat engine, then the maximum thermal efficiency can be estimated using Carnot cycle equation [13, 14] :

$$E_{\max} = \frac{T_{\max} - T_{\min}}{T_{\max}} \times 100\% \quad (9.2)$$

Where $T_{\max}$ is the maximum bed temperature due to combustion of hydrocarbons (K), and $T_{\min}$ is the measured furnace temperature due to heat loss from the reactor wall (K). From Figure 9.12, $T_{\max}$ and $T_{\min}$ are 584 and 200 °C respectively, and $E_{\max}$ is ca. 45 %. This would suggest that RHPE would never reach 100 % due to the constraint of significant heat loss.

After the completion of ATR runs, the reactor was by-passed and the catalyst bed was cooled to ca. 100 °C, a temperature which was far below the light off temperature of mixed hydrocarbons over platinum based catalyst. The third cycle was carried out by admitting gaseous reactants into the reactor. After 5 minutes of time on-line, no sign of oxidation of hydrocarbons occurred. This might be caused by partial deactivation of catalyst active sites induced by the previous oxidation run. The furnace temperature was then increased from 111 °C to 225 °C by heating electrically. Once the bed temperature reached 150 °C, signs of exothermic reaction were obvious (the bed temperature rose to ca. 584 °C) and the furnace temperature controller was quickly turned-off. The axial temperature distribution was measured

and the results are presented in Figure 9.13. Samples of gaseous products from the outlet of the reactor were taken and the results are displayed in Figure 9.14 to 9.16.

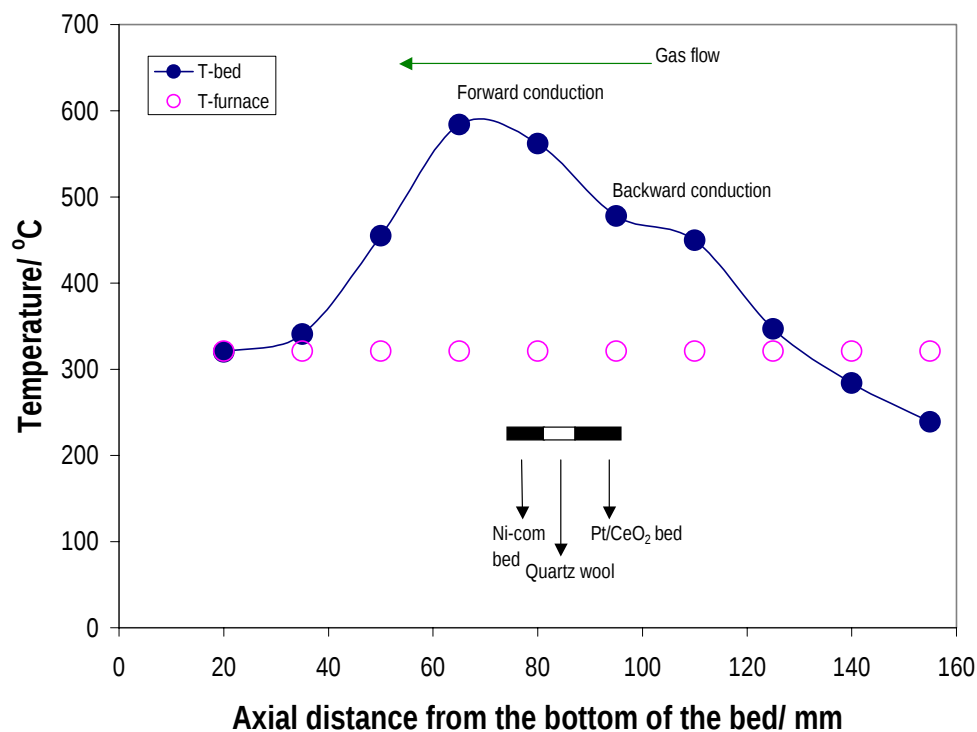


Figure 9.13 Axial temperature distribution during the partial oxidation of artificial gasoline from the third cycle (total dry gas flow 377 mL min^{-1} ; two bed system with total catalyst loaded = 0.5 g)

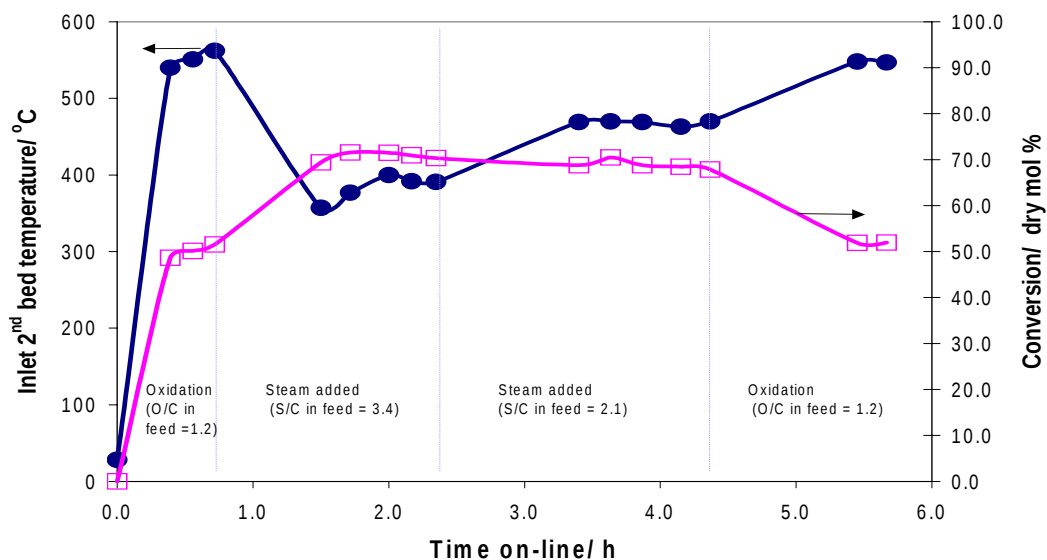


Figure 9.14 Combined catalyst bed temperature and artificial gasoline conversion from second and third cycles (total dry gas flow 377 mL min^{-1} ; two bed system with total catalyst loaded = 0.5 g)

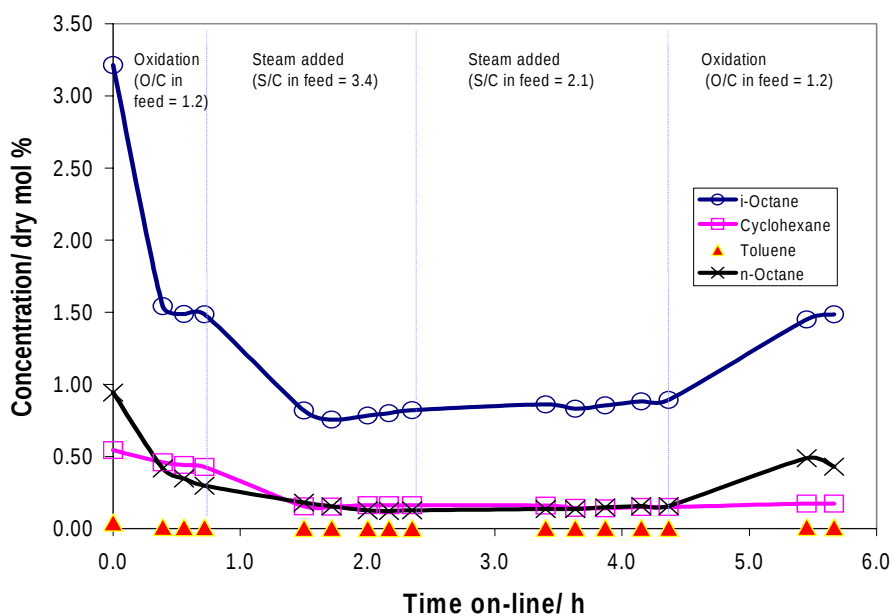


Figure 9.15 Combined concentration profile for the auto thermal reforming of artificial gasoline from second and third cycles (total dry gas flow 377 mL min^{-1} ; two bed system with total catalyst loaded = 0.5 g)

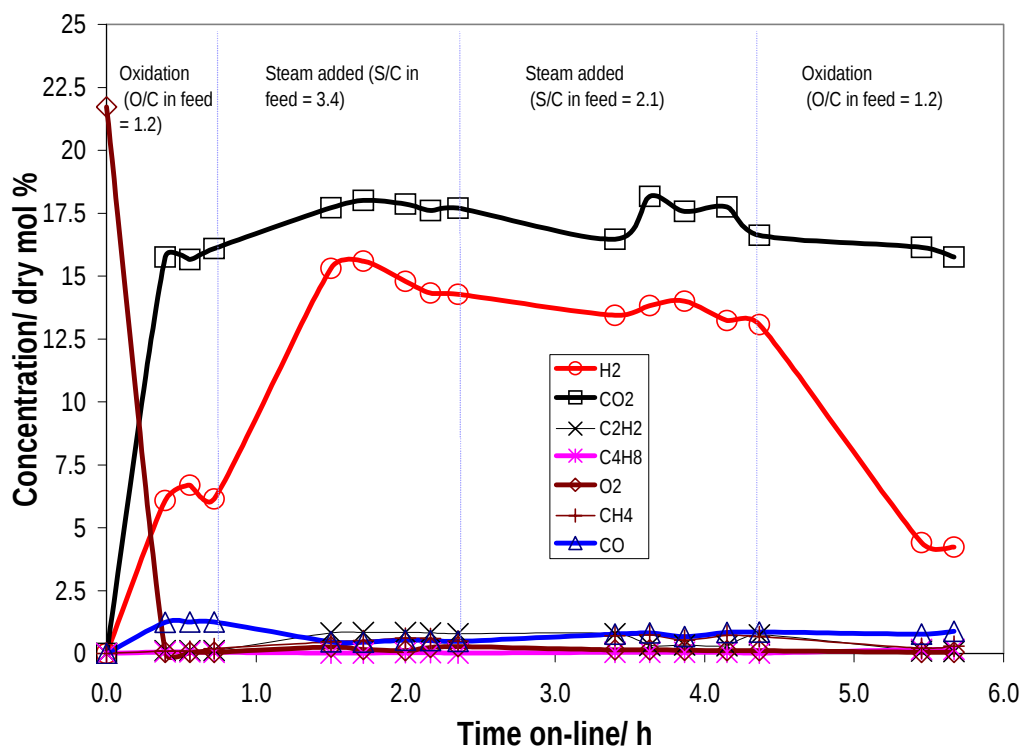


Figure 9.16 Combined product distribution for the auto thermal reforming of artificial gasoline from second and third cycles (total dry gas flow 377 mL min⁻¹; two bed system with total catalyst loaded = 0.5 g)

Figures 9.14 to 9.15 are basically an extension of previous figures. From the third cycle, it could be seen that the overall conversion resulting from the oxidation of hydrocarbons (Figure 9.14 between 5th and 6th hour) was exactly the same as the conversion observed from the second cycle (Figure 9.14 between 0th and 1st hour). However, the amount of hydrogen produced decreased by ca. 30 % based on the initial hydrogen product of ca. 6 dry mol % (Figure 9.16), which might be caused by carbon deposition on the catalyst surface.

After the catalyst bed temperature was brought to ambient, a decoking operation was carried out by passing ca. 71 mL min⁻¹ of 3 % oxygen in nitrogen over the catalyst bed. The bed

temperature was heated from ambient to ca. 600 °C at 5 °C min⁻¹. The progress of decoking was followed by analysis of carbon oxides at the outlet of the reactor as a function of bed temperature. Figure 9.17 depicts the observed results.

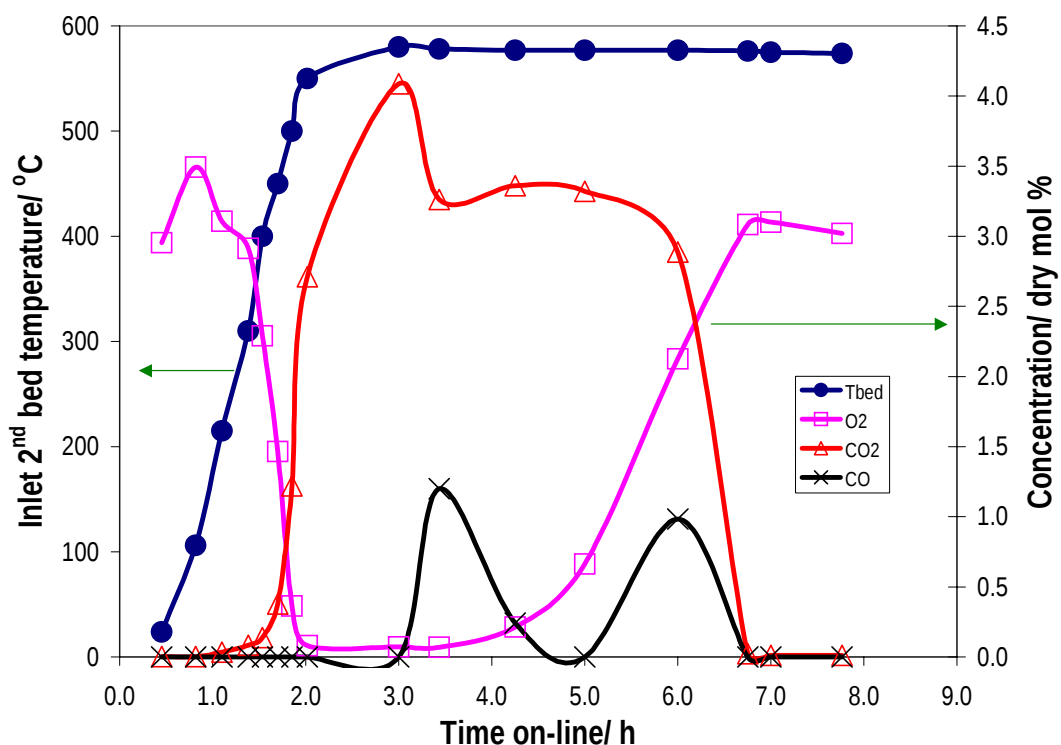


Figure 9.17 Carbon oxides produced by decoking operation (Total flow 71 mL min⁻¹, two bed system with total catalyst loaded = 0.5 g, heating rate 5 °C min⁻¹).

As seen, oxygen was depleted at about 400 °C and was totally used up at ca. above 500 °C. The maximum carbon dioxide peak of 4 % was observed at ca. 575 °C after 3 hours decoking and the concentration was stable at 3 % for about 4 hours. No more carbon dioxide was detected after 7 hours of decoking and, at the same time, the oxygen content was restored to the initial value of 3 %. Whilst the profile of carbon dioxide occurrence followed a volcano

shape, the liberated carbon monoxide was erratic. This could be due to self-oscillation due to oxidation, and this is a well-known phenomenon in CO oxidation studies [15].

Even though the total carbon deposited was a function of all the autothermal reforming runs, it is reasonable to conclude that the major contribution came from the oxidation regime, since unburnt hydrocarbons were subjected to a higher reaction temperature for about one hour and, as a result, thermal cracking might have occurred prior to injecting steam. The relative ease of carbon removal during decoking, along with the constant value of total conversion of hydrocarbons during ATR runs, despite coke formation, indicated that whisker-like carbon might play an important role [12, 16-23].

9.4 Conclusions

Hydrogen production from the autothermal reforming of artificial gasoline has been studied, employed a two-bed catalyst system. Pt/CeO₂ was used to catalyse hydrocarbons combustion, whilst a commercial NiO/MgO catalyst was utilised to catalyse steam reforming of unburnt hydrocarbons.

The reaction system can start to produce hydrogen from ambient temperature. Either hydrogen/air mixtures or electricity can be used as initiators to light off the reaction system at the beginning of operation. However, artificial gasoline/air mixtures only can be used as an initiator when the catalysts are pre-reduced.

Feed compositions play an important role for the attainment of autothermal operations. The oxygen to carbon ratios (O:C) of 1~1.2 and steam to carbon ratios (S:C) of 2~3 gave hydrogen yields of 40~44 % mol/ atom carbon fed and hydrogen selectivities of 66~70 % mol/ atom carbon consumed.

The reaction mechanism involved total oxidation of artificial gasoline (ca. 50 % of gasoline was combusted), followed by steam reforming of unburnt hydrocarbons. Overall, the system was found to produce 3.4~3.6 moles of hydrogen per mole of gasoline fed.

9.5 References

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Chapter 10 Conclusions and recommendations

10.1 Conclusions

Studies of the partial oxidation of isooctane over pre-reduced supported rhodium catalysts showed that the reaction was a two step process: isooctane was first converted into carbon dioxide and steam by total oxidation followed by carbon dioxide and steam reforming of unburnt isooctane. Significant oxidation of isooctane did not occur at ambient temperatures. The initiation temperatures (light off temperatures) for the oxidation of isooctane over Rh/Al₂O₃, Rh/CeO₂-ZrO₂ and Rh/CeO₂- δ Al₂O₃ were observed to lie in the range of 200 – 220 °C, irrespective of the support used. Oxygen was totally consumed at 300 °C. Ceria-zirconia mixed oxides prepared by sol-gel was found to be the preferred support since it did not favour methanation.

Preliminary investigations of the total oxidation of the separate hydrocarbons (cyclohexane, isooctane and 1-hexene) over an unreduced nickel commercial (Ni-com) catalyst at an oxygen:carbon (O:C) ratio of 6 showed that the light-off temperatures of all hydrocarbons tested were above ca. 300 °C. Partial oxidation of cyclohexane at an O:C ratio of ca. 1.5 over the same catalyst increased the light-off temperature by ca. 100 °C (from 350 to 450 °C).

Studies of the partial oxidation of individual liquid hydrocarbons (cyclohexane, isooctane, octane and toluene) over an unreduced Pt/Ni-com catalysts revealed that the light-off temperatures lay between 200 - 225 °C, except for toluene (ca. 265 °C). The order of reactivity of hydrocarbons oxidation followed isooctane > octane > cyclohexane >> toluene.

The use of a CeO₂ support for an unreduced Pt based catalyst remarkably lowered the light-off temperatures of individual liquid hydrocarbons except toluene. The observed light-off temperatures were between 150 – 190 °C (toluene was ca. 265 °C). The order of reactivity followed isooctane > octane > cyclohexane >> toluene.

From the results of oxidation of individual liquid hydrocarbons over unreduced nickel and platinum based catalysts, it was clear that the order of activity of the catalysts followed Pt/CeO₂ > Pt/Ni-com > Ni-com.

Studies of the partial oxidation of artificial gasoline involving mixed liquid hydrocarbons over unreduced Pt/CeO₂ catalysts showed evidence of the importance of relative adsorption strengths. For the mixture of cyclohexane, isooctane, octane and toluene, the order of reactivity followed toluene > octane > cyclohexane > isooctane. For the mixture of 1-hexene, isooctane, octane and toluene, the order of reactivity followed 1-hexene > toluene > octane > isooctane. Stronger adsorption of hydrocarbons such as 1-hexene and toluene led to extensive coverage of metal sites and to preferential oxidation. As a result, the amount of oxygen remaining to oxidise other hydrocarbons was much less, and overall conversion decreased.

Studies of steam reforming for individual hydrocarbons over pre-reduced Ni-com catalysts suggested that hexene and toluene could not be used in the artificial gasoline formulation, due to the higher risk of carbon formation during steam reforming.

The kinetics of steam reforming of isooctane and artificial gasoline (mixed cyclohexane, isooctane and octane) over pre-reduced Ni-com catalysts were studied. Detailed studies of the steam reforming of isooctane and artificial gasoline showed that the reaction was 0.17 order in isooctane and 0.54 order in steam for the temperature range of 310 – 350 °C, whilst the reaction was 0.08 order in *effective* hydrocarbon and 0.23 order in steam for the temperature range of 375 - 425 °C. A reasonable fit to a Langmuir-Hinshelwood model was obtained and showed that the rate determining step for isooctane and hydrocarbon steam reforming probably involved the dual site surface reaction with dissociative adsorption of isooctane (or *effective* hydrocarbon) and steam.

The autothermal reforming of artificial gasoline was finally tested using a laboratory scale tubular reactor. The system could be initiated at a temperature of ca. 175 °C by oxidation of hydrogen at ambient temperature, or by using an electrically heated furnace.

An autoignition of the system at ambient temperature was also successfully demonstrated, provided that the catalyst was pre-reduced. A self-sustaining operation was maintained by oxidising part of the fuel to produce heat for driving steam reforming. The temperatures for both oxidation and steam reforming could be controlled by adjusting an oxygen-nitrogen mixture (simulated air composition) and/ or water to fuel ratios in the feed. Oxygen was used up in the process and hydrogen was produced by partial oxidation and steam reforming reactions.

Competitive adsorption among the individual components of the artificial gasoline was evident.

At an O:C ratio of ca. 1.2 and a S:C ratio of ca. 2, the system produced ca. 3.5 moles hydrogen per mole of gasoline fed. Although the system produced low CO concentration (ca. 0.5 – 0.8 %), there is still a room for further improvement to make the process applicable to proton exchange membrane fuel cell which require less than 10 ppm of CO.

10.2 Recommendations

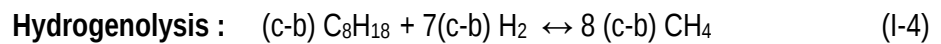
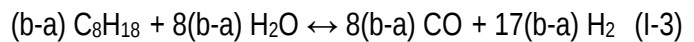
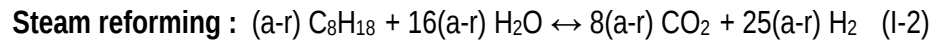
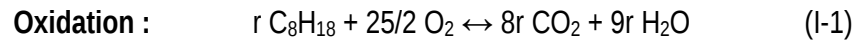
In light of the overall results, the following recommendations for further investigations are suggested:

1. Incorporation of a selective carbon monoxide oxidation reactor to the autothermal reforming system to meet the tolerated carbon monoxide content for fuel cells applications
2. The use of two powerful syringe pumps which have a similar discharge pressure rating, in order to be able to optimise the reactant feeding system
3. The use of a previous fabricated bench-scale reactor as a prototype of an on-board fuel processor
4. Extended studies for the autothermal reforming of diesel fuel
5. The design and testing of a compact fuel processor for on-board vehicles.

Appendix I Calculation of C:O ratio for the partial oxidation of isooctane

A first attempt is prepared, based on the premise that the partial oxidation of hydrocarbon involves total oxidation, steam reforming, and hydrogenolysis reactions [1]. If R is defined as the percentage ratio between actual oxygen concentration in the feed and the oxygen that is stoichiometrically required for isooctane total oxidation, then $r = R/100$.

For 1 mol of isooctane enters the reactor, the following reactions can be written:



Where r, a, b, and c represent mol/mol partial conversions of reactions (I-1), (I-1)+(I-2), (I-1)+(I-2)+(I-3) and (I-1)+(I-2)+(I-3)+(I-4) respectively. The product distribution involves:

$$\text{CO}_2 = 8r + 8(a-r) = 8a$$

$$\text{CO} = 8(b-a)$$

$$\text{CH}_4 = 8(c-b)$$

$$\text{H}_2 = 25(a-r) + 17(b-a) - 7(c-b)$$

$$= 25/8 \text{ CO}_2 + 17/8 \text{ CO} - 7/8 \text{ CH}_4 - 25(R/100)$$

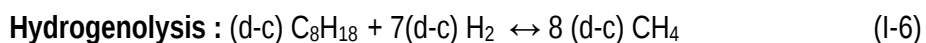
In the absence of hydrogenolysis, the highest conversions are obtained when steam reforming produced CO only, in this case $a = r$. Total conversion of $b = 1$ is achieved if the amount of water produced by reaction (I-1) is sufficient to convert isooctane via reaction (I-3) such that $9r \geq 8(1-r)$ or $r \geq 8/17$. Therefore $R \geq 47\%$.

R is then chosen as 50 % and the respective C:O ratio becomes 1: 1.56. This ratio is used for all partial oxidation runs over Rh-based catalysts (chapter 5).

Since the actual runs indicate some sort of CO₂ reforming of isooctane, the applicability of the C:O ratio is checked by incorporating this complementary reaction.



And the reaction (A-4) should be modified as follows :



Therefore the products distribution are altered:

$$\text{CO} = 8(b-a) + 16(c-b)$$

$$\text{CH}_4 = 8(d-c)$$

$$H_2 = 25(a-r) + 17(b-a) + 9(c-b) - 7(d-c)$$

d represents total conversion of isooctane by summing-up reaction (I-1) to (I-6) minus (I-5). Once again, in the absence of hydrogenolysis, isooctane conversion hits the highest level if steam reforming produces CO only ($a = r$). Moreover, c (sum of reactions I-1 to I-5) = 1 if the amount of water and CO₂ produced by reaction (I-1) are enough for total transformation of isooctane via reaction (I-3) and (I-5). Therefore two un-equalities are existent:

$$9r \geq 8(b-a) \text{ or } 9r \geq 8(b-r) \text{ and}$$

$$8r \geq 8(c-b) \text{ or } 8r \geq 8(1-b)$$

Solving for r yields: $r \geq 8/25$ or $R \geq 32\%$, and the initial R of 50 % is more than adequate to favour partial oxidation of isooctane.

Note that all derived equations are based on the carbon oxides methanation FREE reaction as demonstrated by Rh/CeO₂-ZrO₂ catalyst.

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Appendix II Analysis of ratios for the partial oxidation and related reactions of isooctane over Rh/CeO₂-ZrO₂ catalyst

Given that the partial oxidation of isooctane involves the following reactions:



The ratio of (H₂/CO)_(II-2) = 2.1 while (H₂/CO)_(II-3) = 0.6. The average value of this ratio = 1.4.

If α is defined as the contribution of (H₂/CO) ratio based on steam reforming, one can

obtain: $\alpha(2.1) + (1 - \alpha)(0.6) = 1.4$, thus $\alpha = 0.53$.

If β = experimental values of (H₂/CO) ratios over Rh/CeO₂-ZrO₂ catalyst (best support) at various temperatures (Chapter 5), then the following table is prepared

Temperature/ °C	β	α	Remarks
400	2.6	1.3	Dry reforming non-existent
450	2.2	1.1	Dry reforming non-existent
500	1.9	0.9	Dry reforming non-existent
600	1.4	0.5	Steam and dry reforming existent

Appendix III Treatment of results

1. *Establishment of material balances*

The following mass balances are derived based on the isooctane or octane, which can be applied either for the partial oxidation or steam reforming reaction. Nitrogen is used as a tie gas and a carbon-free operation is assumed.

Nitrogen balances: $F_o = N_{in}/Y_{No}$

Carbon balances: $C_{in} = F_o (Y_{CO} + Y_{CO_2} + Y_{CH_4} + 2Y_{C_2H_2} + 8Y_{C_8H_{18}})$

Where Y_i = mole fraction of component i in the dry effluent

F_o = dry effluent flow rate, mole min^{-1}

N_{in} = inlet nitrogen flow rate, mole min^{-1}

C_{in} = inlet carbon flow rate, atom min^{-1}

The measured flow rate (mole min^{-1}) is obtained by the following equation

$$F'_o = F_o / (22.4 \times 10^3)$$

$$C_8H_{18} \text{ in} = C_{in} \times 8$$

(C_8H_{18} in) as measured by FID response is in agreement within $\pm 5\%$ in comparison to calculated (C_8H_{18} in) by carbon balances.

2. *Fuel conversion calculation*

The overall conversion of isooctane (oxidation and steam reforming) can be calculated from carbon balances

$$x = \frac{(CO) + (CO_2) + (CH_4) + 2(C_2H_2)}{(CO) + (CO_2) + (CH_4) + 2(C_2H_2) + 8(C_8H_{18})} \times 100\%$$

(i) = effluent flow rate of component i (mole min^{-1})

The conversion of individual compound of the artificially mixed gasoline is calculated by the following formula

$$X_i = \frac{(HC_i)_{in} - (HC_i)_{out}}{(HC_i)_{in}} * 100\%$$

(HC_i) = The molar flow rate of compound i (mole min^{-1})

3. *Hydrogen yield*

In general, hydrogen yield is defined as (moles of observed H_2)/(moles of hydrocarbon fed) * 100%, except that, in Chapter 5, the denominator is the calculated hydrogen by thermodynamics.

4. *Hydrogen selectivity*

$$S_{H_2} = \frac{(H_2)_{observed}}{(Carbon)_{consumed}} * 100\%$$

() = moles or atom min^{-1}

The carbon atom is used rather than hydrocarbon compound, due to the fact that, in the artificially mixed gasoline, hydrogen is produced by partial oxidation and/ or steam reforming of mixed hydrocarbons.

5. *Reaction rates*

The rate of isooctane (as an example) disappearance is calculated from the following equation

$$-r = \frac{(C_8H_{18}) * X_{C_8H_{18}}}{100 * W_{cat}}$$

() = the molar flow rate (mole s⁻¹)

W_{cat} = catalyst weight excluding diluent (g)

X_{C₈H₁₈} = the conversion of isooctane

Appendix IV Adiabatic temperature rise for isooctane in N_2

Given 1 mol isooctane in 99 mol nitrogen.

Heat of combustion of isooctane = 5460 kJ mol^{-1}

Heat capacity of nitrogen = $29 \text{ J K}^{-1} \text{ mol}^{-1}$

Ninety mol nitrogen require $29 \times 99 \text{ J}$ to raise 1 K, thus

$$\Delta T = (5460 \times 10^3) / (29 \times 99) \approx 1900 \text{ K}$$

Appendix V The stoichiometric calculation for the autothermal reforming of artificial gasoline

The autothermal reforming of artificial gasoline involves combustion of part of the fuel to supply heat and steam to drive steam reforming of unburnt gasoline. The objectives of the following calculations are

- (i) To obtain amounts of gasoline combusted as a function of O:C (R) ratios in feed
- (ii) To estimate amounts of additional steam to be injected, in order to attain an optimum value of hydrogen product

$$\text{Given that: } C_xH_y + (x+y/4) O_2 \leftrightarrow x CO_2 + y/2 H_2O \quad (V-1)$$

With the initial conditions (molar flow rates) of

$$C_xH_y = F; O_2 = \frac{1}{2} F R x; CO_2 = 0 \text{ and } H_2O = 0.$$

When all of oxygen fed is used up, the final flow rates involve

$$C_xH_y = F - \frac{1}{2} F R x / (x + y/4); CO_2 = \frac{1}{2} F R x \cdot x / (x + y/4) \text{ and } H_2O = \frac{1}{2} F R x \cdot \frac{1}{2} y / (x + y/4).$$

Since amounts of gasoline combusted is the difference between initial and final flow rates of gasoline, therefore

$$X_c(\text{conversion}) = (1 - \frac{1}{2} R x / (x + y/4)) * 100\% \quad (V-2)$$

For isooctane ($x = 8$; $y = 18$), the equation (V-2) yields $X_{\text{isooctane}} = (1 - 0.32 R) * 100\%$.

In order to obtain an optimum value of hydrogen product, an optimum S:C ratio (S_{opt}) is required. As a result, more steam (F_s) should be added in the system to give

Total steam = $F_s + \frac{1}{2} F R x \cdot \frac{1}{2} y/(x+y/4)$, whilst

Total C = $x F(1 - \frac{1}{2} R x/(x + y/4))$

$$S_{opt} = \{ F_s + \frac{1}{2} F R x \cdot \frac{1}{2} y/(x+y/4) \} / \{ x F(1 - \frac{1}{2} R x/(x + y/4)) \} \quad (V-3)$$

Or

$$F_s = S_{opt} F x (1 - \frac{1}{2} R x/(x + y/4)) - \frac{1}{4} F R x y/(x + y/4)$$

Thus, s:c ratio (S_f) in feed can be obtained

$S_f = F_s/(F \cdot x)$ which leads to the final equation of

$$S_f = S_{opt} (1 - \frac{R \cdot x}{2(x + \frac{y}{4})}) - \frac{R \cdot y}{4(x + \frac{y}{4})} \quad (V-4)$$

For isooctane with $R = 1$ and $S_{opt} = 3$, equation (V-4) yields

$$S_f = 3 (1 - 0.32) - 0.36 = 1.68$$

As a result, a steam:carbon ratio of ~ 2 in feed is a reasonable estimate for the attainment of an optimum value of hydrogen product.

Appendix VI Isooctane combustion in a pseudo adiabatic reactor

The amount of isooctane to be burnt in order to raise the catalyst bed temperature to ca. 873 K (600 °C) is estimated, based on the previous preliminary results for autothermal reforming of isooctane over Pt/Ni-com catalyst.

$$\text{Isooctane fed} = 0.023 \text{ mol h}^{-1}$$

$$\text{Unburnt isooctane} = 0.0099 \text{ mol h}^{-1}$$

$$\text{Isooctane combusted} = 0.0131 \text{ mol h}^{-1} \text{ (} T_{\text{max}} \text{ observed} = 382 \text{ °C (655 K))}$$

$$\text{Thus, amounts of isooctane to be combusted} \approx (873/655) \times 0.0131 = 0.0175 \text{ mol h}^{-1}.$$

$$\text{Oxygen required} = (12.5/1) \times 0.0175 = 0.22 \text{ mol h}^{-1}.$$

$$\text{Air required} = (0.22/0.21) = 1.05 \text{ mol h}^{-1}.$$

For safety reason, 6.5 % < isooctane < 2 %.

Say that isooctane fed = 10 % in air.

$$\text{Therefore, isooctane fed} = (0.1/0.9) \times 1.05 = 0.12 \text{ mol h}^{-1}.$$

$$\text{Carbon fed} = 8 \times 0.12 = 0.96 \text{ mol h}^{-1}.$$

$$\text{R (O:C ratio)} = (2 \times 0.22)/0.96 = 0.46$$

Amounts of steam:carbon ratio required in the feed, S_f , can be estimated as follows (Appendix V)

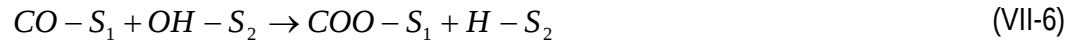
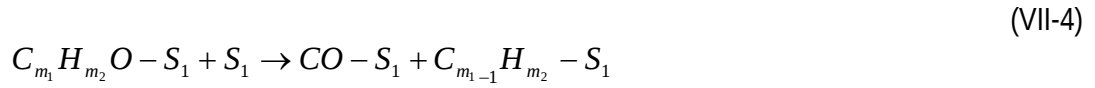
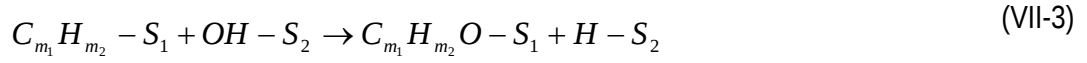
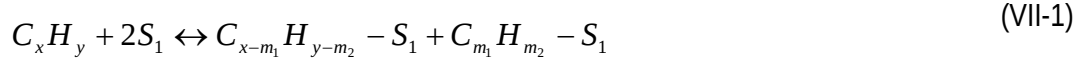
$$S_f = S_{\text{opt}} (1 - 0.32 R) - 0.36 R, \text{ thus}$$

$$S_f = 3 (1 - 0.32 \times 0.46) - 0.36 \times 0.46 = 2.39.$$

Where S_{opt} is the optimum steam:carbon ratio in the system. Thus, the steam:carbon ratio required in the feed is between 2 – 3. Once the amount of hydrocarbon fed is established, the water to be fed in the system can be estimated.

Appendix VII The derivation of Langmuir-Hinshelwood (LH) kinetics of model 3

A general mechanism for hydrocarbon steam reforming may involve [1]



where m is integer.

Equations (VII-1) to (VII-3) can be re-written as



Further more

$$K_A p_A \theta_1^2 = \theta_C \theta_D$$

Assuming $\theta_C = \theta_D$ yields

$$\theta_C = \theta_1 \sqrt{(K_A p_A)}$$

Site balance around S_1 yields

$$1 = \theta_1 + \theta_C + \theta_D$$

Suppose that θ_C is MARI (the most reactive intermediate), then

$$\theta_1 = (1 + \sqrt{K_A p_A})^{-1}$$

Similar treatment to equation (VII-2-1) yields

$$\theta_B = \theta_2 \sqrt{K_B p_B}, \text{ thus}$$

$$\theta_2 = (1 + \sqrt{K_B p_B})^{-1}$$

Let that equation (VII-3-1) is the rate determining step, thus

$$-r = k \theta_A \theta_B$$

Finally, formal LH considerations immediately leads to the following model 3

$$-r = \frac{k_{rxn} \sqrt{p_A p_B}}{(1 + \sqrt{K_A p_A})(1 + \sqrt{K_B p_B})} \quad (\text{VII-9})$$

where $k_{rxn} = k \sqrt{K_A K_B}$.

1. Adesina, A.A., *Personal communication*. 2003: Sydney.

Appendix VIII Estimation of error propagation

Reference is made to Adesina's work [1] in estimating errors in the specific reaction rate.

Given a general formula

$$Y = f(X_i) \quad (\text{VIII-1})$$

where X_i are the independent variables, then the fractional error incurred by the dependent variable, Y , due to errors in X is expressed as follows

$$\left(\frac{\Delta Y}{Y}\right)^2 = \sum \left(\frac{d \ln Y}{d \ln X_i}\right)^2 \left(\frac{\Delta X_i}{X_i}\right)^2 \quad (\text{VIII-2})$$

since

$$r = \frac{FC}{W} \quad (\text{VIII-3})$$

where, r is the specific reaction rate ($\text{mole g}^{-1} \text{s}^{-1}$)

F is the feed flow rate across the reactor (mole s^{-1})

C is the feed conversion (%)

W is the catalyst weight (g)

Taking natural logarithms of both sides of equation (VIII-3) one obtains

$$\ln r = \ln F + \ln C - \ln W \quad \text{and}$$

$$\frac{d \ln r}{d \ln F} = \frac{d \ln r}{d \ln C} = -\frac{d \ln r}{d \ln W} = 1 \quad (\text{VIII-4})$$

From equation (VIII-2) one may write

$$\left(\frac{\Delta r}{r}\right)^2 = \left(\frac{\Delta F}{F}\right)^2 + \left(\frac{\Delta C}{C}\right)^2 + \left(\frac{\Delta W}{W}\right)^2 \quad (\text{VIII-5})$$

According to the manufacturer's specification of the instruments and the repeated experimental measurements carried out, the following values are obtained

$$\frac{\Delta F}{F} = 0.5 - 1\%$$

$$\frac{\Delta C}{C} = 1.5 - 2\%$$

$$\frac{\Delta W}{W} = 0.6 - 1.2\%$$

Therefore the lower (LL) and upper (UL) limits of $\frac{\Delta r}{r}$ can be estimated by equation (VIII-5)

$$\text{LL} : \frac{\Delta r}{r} = \left[(5 \times 10^{-3})^2 + (6 \times 10^{-3})^2 + (1.5 \times 10^{-2})^2 \right]^{0.5} = 0.017$$

$$\text{UL} : \frac{\Delta r}{r} = \left[(1 \times 10^{-2})^2 + (1.2 \times 10^{-2})^2 + (2 \times 10^{-2})^2 \right]^{0.5} = 0.025$$

Thus, the expected error range of the reaction rate is 1.7 – 2.5 %

1. Adesina, A.A., *PhD Thesis*. 1986, University of Waterloo: Canada.