

Adiabatic Diesel Pre-reforming

Literature Survey

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Acknowledgement/Preface

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Abstract

A literature review of adiabatic pre-reforming of diesel is presented. By far the largest body of literature on heavy feedstock pre-reforming deals with nickel based catalysts. Nickel is relatively inexpensive while still very active for reforming reactions. Nickel catalysts are in industrial operation in numerous pre-reformers and steam reformers worldwide. Kinetics, catalyst activity, and deactivation all depend strongly on feedstock, process conditions and nature of the catalyst. In general, the process is operated at space velocities of 1,500 – 3,000 hr⁻¹. The adiabatic pre-reforming process is based on a set of reactions: steam reforming of hydrocarbons, followed by water-gas shift and methanation reactions. Steam reforming is irreversible for all higher hydrocarbons. No intermediate products are generally formed and complete conversion is normally be attained. The only exceptions are light hydrocarbons (ethane, propane, etc.) that may be formed during cracking reactions at elevated temperatures as well as benzene, which has been observed by a number of authors and possibly is a reaction intermediate. Water-gas shift and methanation are limited by thermodynamic equilibrium.

Main issues with pre-reforming of heavy feedstock over nickel catalysts are related to catalyst deactivation by sulphur poisoning and coke deposition. Even desulphurised diesel may contain up to 1 ppm of sulphur and sulphur strongly and selectively poisons active nickel sites. Sulphur poisoning causes progressive deactivation in the catalyst bed. The deposition of carbonaceous species is strongly related to the feedstock used. Large and/or unsaturated hydrocarbons adsorb strongly on the catalyst surface and may easily form gum deposits. Gum deposits are formed at relatively low temperatures and may cause very fast catalyst deactivation by encapsulation of active sites. Typically for nickel based catalysts, carbon whiskers may be formed at high temperatures and low steam ratios. Whiskers do not directly affect the catalyst activity, yet may eventually break down catalyst particles and cause plugging of the reactor. The temperature window between gum and whisker formation determines the operating temperature for the pre-reforming process. Based on a number of publications, it appears possible to operate an adiabatic diesel pre-reformer in such conditions that the deactivation rate by sulphur poisoning and by coke deposition is acceptably low. After an initial period of more rapid deactivation, the deactivation appears to stabilise at a 'resistance number' of 5–20 kg/g (kilogram of feedstock per gram of catalyst deactivated).

Precious metal catalysts may be a valid alternative to common nickel based catalysts. Among the potential benefits encountered in literature are a higher activity, better sulphur tolerance, and an enhanced coking resistance, while the main drawback is related to the price of precious metals. As with nickel, kinetics, catalyst activity, and deactivation all strongly depend on feedstock, process conditions and nature of the catalyst. In contrast to nickel, catalysts based on platinum, rhodium, and ruthenium form little or no carbon filaments. Other types of carbonaceous deposits, however, are still formed and effectively determined the window of operation for a given feedstock. Unfortunately, data on the occurrence or prevention of gum formation on precious metal catalysts is effectively lacking, as are data on the deactivation rates that may be expected over the lifetime of a precious metal pre-reforming catalyst.

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Summary

The pre-reforming process converts higher hydrocarbons into a mixture of hydrogen and C₁ components: CO, CO₂, and methane. It reduces the risk of coke formation in downstream reforming processes. Pre-reforming is practiced at industrial scales with hydrocarbon fuels ranging from natural gas up to naphtha. More recently, attention has been drawn to pre-reforming at small scales or with heavier feedstock such as diesel. Direct steam reforming of heavy hydrocarbon fuels may cause severe carbon deposition problems at elevated temperature. Because it has a lower operating temperature, pre-reforming may be required in order to achieve a stable process.

The adiabatic pre-reforming process is based on a set of reactions: steam reforming of hydrocarbons, followed by water-gas shift and methanation reactions. Steam reforming is irreversible for all higher hydrocarbons. No intermediate products are generally formed and complete conversion is normally be attained. Water-gas shift and methanation are limited by thermodynamic equilibrium. While steam reforming is strongly endothermic, water-gas shift and methanation are exothermic. The overall heat of reaction may therefore be negative, zero, or positive and the process, in contrast to other reforming processes, can be operated adiabatically. For heavy feedstock such as diesel, this results in a characteristic temperature profile. It displays a decrease in temperature followed by an increase in temperature along the reactor axis. The shape of the temperature profile depends on the nature of the feedstock and the operating pressure (which affects the equilibrium of methanation). The shape of the axial temperature profile changes during the process, because of catalyst deactivation, which cannot normally be prevented. As a result, the temperature profile moves along the reactor axis in the direction of flow, while the width of the profile broadens.

Group VIII metals are catalytically active for the steam reforming reaction. Nickel is the active metal in almost all industrial catalysts. Precious metals are very active for the steam reforming as well. Mechanistic and kinetic studies can be found in literature for both classes of catalysts. Precious metals may offer advantages in terms of a better sulphur tolerance and reduced rates of coking. Nevertheless, both nickel and precious metal pre-reforming catalysts degrade over time. Critical issues are the poisoning by sulphur and the formation of carbonaceous deposits, in particular gum at low temperatures and whiskers at higher temperatures. The limits of gum and whisker formation result in a temperature window, in which a catalyst can be operated at acceptable deactivation rates. As the deactivation of nickel catalysts at favourable operating conditions approaches a constant rate over time, predictive modelling is possible. For precious metal catalysts, deactivation data is largely lacking.

1. Adiabatic Diesel Pre-reforming

The development of fuel cell systems has created a small scale demand for hydrogen and/or synthesis gas. No large-scale infrastructure is presently available for the distribution of hydrogen or synthesis gas. While sustainability will eventually stipulate renewable energy sources, an economically efficient phase in the transition towards sustainability will make use of the available infrastructure for fossil fuels and locally generate hydrogen or synthesis gas through reforming. (Uyterlinde, 2007)

The reforming process converts conventional fuels, ranging from natural gas through LPG and gasoline to diesel, into hydrogen rich gases that are suitable for fuel cells. While natural gas and LPG are converted relatively easy, liquid fuels are much more difficult to reform efficiently and stable. They are a complex mixture of hydrocarbon compounds containing saturates, olefins, and aromatics. The boiling range of the constituents makes fuel introduction, evaporation, and mixing difficult. Vaporisation might not be possible because of pyrolysis and coking at elevated temperatures. Nevertheless, liquid fuels such as gasoline and diesel are globally attractive because of their existing infrastructure, higher well-to-wheel efficiencies, and higher energy densities. (Shekawat, 2006)

The pre-reforming process converts higher hydrocarbons into a mixture of hydrogen and C₁ components CO, CO₂, and methane. It reduces the risk of coke formation in downstream reforming processes. Because of the subsequent endothermic and exothermic reactions involved (Section 1.2), the process can be operated adiabatically in contrast to the actual reforming process downstream. Adiabatic pre-reforming is practiced at industrial scales with hydrocarbon fuels ranging from natural gas up to naphtha. (Christensen, 1996) More recently, attention has been drawn to pre-reforming at small scales or with heavier feedstock such as diesel. (Piwetz, Larsen & Christensen, 1996; Rostrup-Nielsen, Christensen & Dybkjaer, 1998)

1.1 Adiabatic Pre-reforming

The adiabatic pre-reforming process is widely used in the chemical process industry. It is used in the production of synthesis gas and/or hydrogen in refineries; it is part of methanol and ammonia synthesis plants and it plays a role in the synthesis of many bulk chemicals. (Christensen, 1996; Christensen, Rostrup-Nielsen, 1996)

The pre-reforming process was developed initially for the production of methane-rich gases for use as town gas and synthetic natural gas. Presently, adiabatic pre-reforming is used industrially for conversion of higher hydrocarbons, allowing for more stringent operating conditions in the downstream (reforming) equipment.

1.1.1 Historical Development

The first industrial steam reformer was installed by Standard Oil of New Jersey at Baton Rouge, where it was commissioned in 1930. The reforming process was then largely adopted in the USA, where natural gas was an abundant feedstock. In the 1950s the first shift towards heavier feedstock was made in Europe, where light distillate naphthas became an economical feedstock. Naphtha was reformed either in steam reforming or in adiabatic gasification. The latter was developed as the catalytic rich gas (CRG) process in the 1950s and 1960s by the British Gas Council on the one hand and by BASF/Lurgi on the other. (Jockel, 1969; Rostrup-Nielsen, 1984) It can be regarded as the predecessor of current pre-reforming processes. With a feed of steam, gasoline or naphtha, and hydrogen and inlet temperatures in the range of 380 – 420°C at a pressure of 15 – 35 atm, a mixture of C₁ components and hydrogen is produced. (Jockel, 1969; Jockel, Supp & Krumm, 1970) A typical temperature profile is observed, with initially a de-

crease in temperature (15 – 20°C below inlet temperature) and subsequently an increase in temperature (outlet 20 – 60°C above inlet). Polymerisation products were identified to cause deactivation of the high nickel catalyst. (Jockel, 1969)

1.1.2 Pre-reforming Process for Heavy Hydrocarbons

While a number of sources (Cerini, Shah & Voecks, 1977; O'Hara, 1986; Ming, 2002; Harasti, 2004; Dalla Betta, Messersmith & Yee, 2005; Konrad, 2005; Cheekatamarla, Thomson, 2006; Goud, 2007; Thormann, 2008) report the direct steam reforming of heavy hydrocarbon fuels, problems are to be expected due to carbon deposition at elevated temperature. Reforming at elevated temperatures may yield graphitic whiskers on the catalyst or even pyrolytic carbon from precursors that are formed above 650°C. (Rostrup-Nielsen, 1984)(Section 4.2) Because it has a lower operating temperature, pre-reforming may be required in order to achieve a stable process.

Pre-reforming requires an extra unit operation in the fuel processing train but it has a number of advantages. In adiabatic pre-reforming all higher hydrocarbons are converted completely into CH₄, CO, CO₂, and H₂. Depending on the feedstock and allowable steam to carbon ratio, inlet temperatures are generally in the range of 350 – 550°C. At these low temperatures, any traces of sulphur that may be left in the feedstock after desulphurisation are effectively adsorbed, at least on common nickel pre-reforming catalysts. Downstream processes will not suffer from sulphur poisoning (but of course sulphur poisoning of the pre-reforming process must still be dealt with). Because all higher hydrocarbons are converted in adiabatic pre-reforming, the risk of olefin formation by steam cracking is eliminated and the product gas can be safely heated up to 700°C or higher without the risk of coke deposition. (Dybkjær, Madsen, 1998; Krummrich, 2006) Therefore, the steam reformer can be operated smoothly at high temperatures, allowing for high space velocities. For example, Chen et al. (2006a; 2006b) attributed a higher stability of the downstream autothermal reformer to the presence of an adiabatic pre-reformer. In addition, the high sensitivity of the steam reforming process to variations in the (local) steam to carbon ratio is significantly diminished. Finally, pre-reforming practically eliminates any variations in the composition of the feedstock.

These considerations are based on industrial scale processes but they largely remain valid for smaller scale fuel processing. As mentioned above, the current focus is on the reforming of diesel fuel for fuel cell applications. In adiabatic pre-reforming, feedstock ranging from natural gas to naphtha is processed on industrial scale but pilot plant tests have revealed that even diesel can be successfully pre-reformed. (Piwetz, Larsen & Christensen, 1996; Christensen, 1996) However, even low-sulphur diesel contains sulphur in the ppm range and pre-reforming, being a low temperature process often based on nickel catalysts, can be very sensitive to sulphur poisoning. Pre-reforming of diesel could consequently require severe desulphurisation down to ppb level, adding to complexity and cost. On the other hand, a nickel pre-reforming catalyst will generally absorb all traces of sulphur left in the feedstock and thereby effectively protect all downstream equipment from sulphur poisoning. More recently, an increased interest in precious metal catalysts is observed, including studies suggesting a relatively high sulphur tolerance. (Zheng, Strohm & Song, 2003; Strohm, Zheng & Song, 2006; Lu, 2008)

A critical issue in diesel pre-reforming is the introduction of fuel. Being a liquid of a wide as well as high boiling range, steady evaporation and mixing with the other reactants is not evident. Evaporation of diesel brings about the risk of thermal cracking. The cracking reactions, however, can be minimised by proper evaporator design and operating conditions. (Krummrich, 2006) Insufficient evaporation, on the other hand, may lead to the deposition of carbonaceous deposits in the system and eventually to plugging. Evaporation of diesel is preferably done through heating of a spray of small droplets in order to achieve a constant mixture of pre-reformer feed. (Autenrieth, 2001) InnovaTek have developed a miniature diesel steam reformer for 1-5kW_e applications. Special attention has been given to the design of a proper fuel injector

was developed, which is claimed to have good mixing and evaporation characteristics. (Ming, 2005)

There is not always need to convert the feedstock into hydrogen completely. For instance, high temperature fuel cells can be fuelled by hydrogen and carbon monoxide while they may be able to internally reform methane internally. Therefore, these fuel cells can be operated on liquid hydrocarbon feedstock after a single pre-reforming step. (Aicher, 2006; Foger, Ahmed, 2005)

1.1.3 Current commercial Interests

Pre-reforming is an economically important process, which is reflected in the number of catalyst manufacturers involved. Table 1.1 lists a selection of the pre-reforming catalysts of major catalyst producers that are suitable for heavy feedstock.

Table 1.1 *Selected commercial pre-reforming catalysts for pre-reforming or heavy feedstock (open literature only)*

Supplier	Commercial name	Feedstock / application	Active metal wt%	Promoter wt%	Carrier
Haldor Topsøe (Haldor Topsøe, 2001; Shekawat, 2006)	RKNGR	NG, LPG, naphtha; aromatics up to 30 wt%	NiO: 25	–	MgO, Al ₂ O ₃
Johnson Matthey / Katalco (Abbott, McKenna, 2005; Shekawat, 2006)	46-3Q	Naphtha	NiO: 23	K ₂ O: 7 Na ₂ O: <0.5	CaAl ₂ O ₄ , ZrO ₂ , SiO ₂
	46-5Q	Light HC and naphtha	NiO: 20	K ₂ O: 1.8	CaAl ₂ O ₄ , SiO ₂
	46-6Q CRG-F CRG-LH	Naphtha	NiO: 16	–	CaAl ₂ O ₄
Süd-Chemie (Shekawat, 2006; Süd-Chemie, 2005)	ReforMax 100	NG – naphtha	NiO: 56		balance
	C11-NK	Naphtha	NiO: 25	K ₂ O: 8.5	CaAl ₂ O ₄
Unicat (Unicat Catalyst Technologies, 2007; Shekawat, 2006)	NGPR-1	Pre-reforming “light to medium severity applications”	NiO: 25	trace	MgAl ₂ O ₄

InnovaTek have developed a proprietary catalyst for the steam reforming of liquid fuels, with enhanced resistance to coking and sulphur poisoning. (Ming, 2002) The catalyst, called ITC, consists of a bimetallic compound supported on a high surface area alumina, treated with an oxygen ion conductor. It has been tested with gasoline, hexadecane, and diesel. (Ming, 2005)

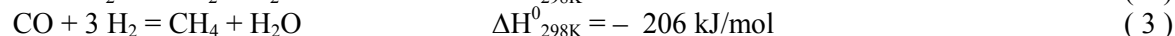
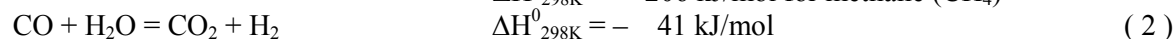
1.2 Diesel Pre-reforming Chemistry

In pre-reforming, higher hydrocarbons react with steam to form a mixture of C₁-components and hydrogen. For heavier feedstock such as diesel, catalyst stability generally requires additional hydrogen to be supplied to the process as well. The adiabatic pre-reforming process is based on a set of reactions: steam reforming of hydrocarbons (1), followed by water-gas shift (2) and methanation (3) reactions. (Christensen, 1996; Christensen, Rostrup-Nielsen, 1996; Roine, 2002)



$$\Delta H_{298K}^0 = +2045 \text{ kJ/mol for 1-Tetradecene (C}_{14}\text{H}_{28})$$

$$\Delta H_{298K}^0 = + 206 \text{ kJ/mol for methane (CH}_4\text{)}$$



Reaction (1) is irreversible for all higher hydrocarbons ($n > 1$) no intermediate products are formed and, provided sufficient catalyst activity is present in the reactor, complete conversion will be attained. Reactions (2) and (3) are limited by thermodynamic equilibrium.

While reaction (1) is strongly endothermic, reactions (2) and (3) are exothermic. The overall heat of reaction may therefore be negative, zero, or positive. For heavy feedstock such as diesel, this results in a characteristic temperature profile in an adiabatic reactor, see Figure 1.1. It displays a decrease in temperature followed by an increase in temperature along the reactor axis. No radial temperature gradients are normally present. (Christensen, 1996) The shape of the temperature profile depends on the nature of the feedstock (for reaction (1), the enthalpy per mole of carbon decreases from 206 kJ/mol-C for methane to 146 kJ/mol-C for $C_{14}H_{28}$) and the operating pressure (which affects the equilibrium composition of (3)). The shape of the axial temperature profile is altered during the process, because of catalyst deactivation, which cannot normally be prevented. As a result, the temperature profile moves along the reactor axis in the direction of flow, while the width of the profile broadens.

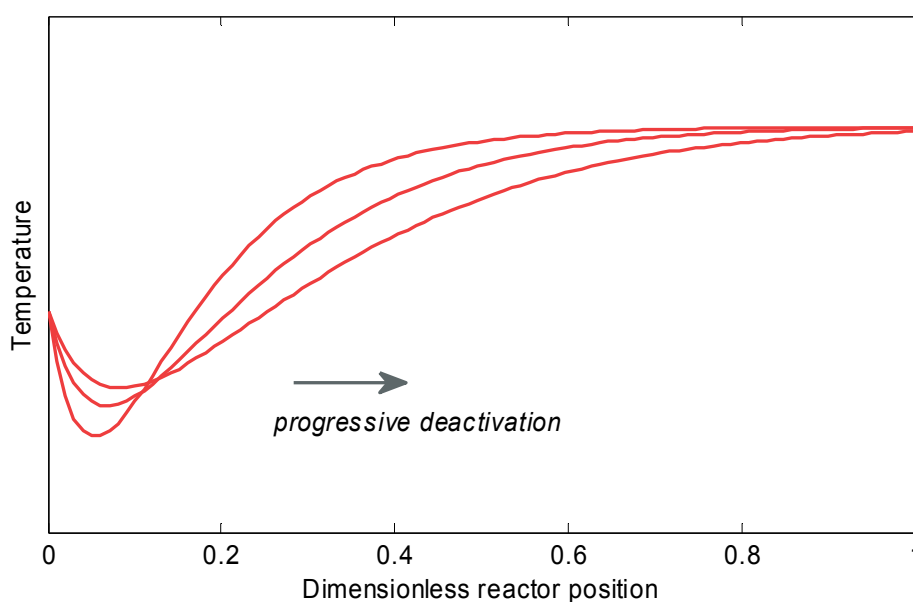


Figure 1.1 *Typical axial temperature profile in an adiabatic diesel pre-reformer*

1.2.1 Feedstock

Any given feedstock for pre-reforming will require a specific operating window. Important process parameters such as the temperature limits, steam to carbon ratio, and amount of hydrogen to be fed all strongly depend upon the feedstock composition. Natural gas is readily pre-reformed at an industrial scale, but heavier fuels such as naphtha, kerosene, or even diesel make it increasingly difficult to attain sufficient catalyst stability for a technically and economically attractive process.

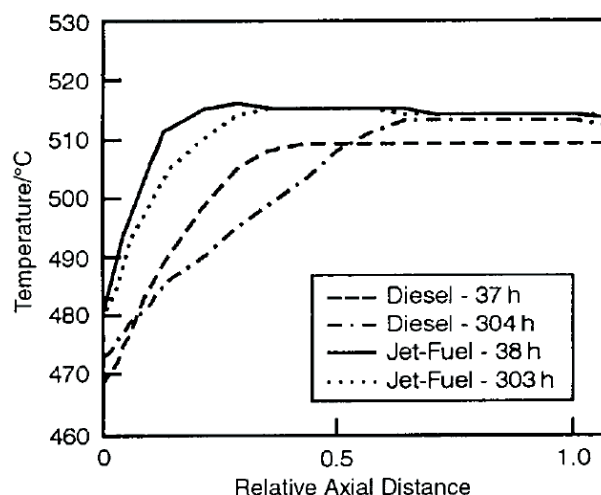
Higher alkanes have bond energies in the range of 350–400 kJ/mol for C-H bonds and about 320 kJ/mol for C-C bonds. Transition metals activate hydrocarbons at temperatures as low as

370-570 K and breakage of the C-C bond on nickel starts at low temperatures. (Rostrup-Nielsen, 1984) Studies on pure hydrocarbons have shown that hydrocarbons in naphtha are more reactive than methane, with the notable exception of benzene and aromatics. (Rostrup-Nielsen, Tottrup, 1979) Consequently, the reactivity of full-range naphtha is less than that of light naphtha, and the reactivity of diesel is less than that of naphtha. Unfortunately, unsaturated hydrocarbons such as aromatics, which make up a fairly large part of diesel fuel, are also the most critical with respect to coke formation. In terms of the simplified mechanism to be proposed in Section 4.2.5, ethylene and benzene chemisorb more easily and hydrocrack less easily compared to paraffins. Consequently, diesel fuel has a very high risk of coke deposition. (Rostrup-Nielsen, Tottrup, 1979)

Adiabatic pre-reforming of heavy fuels suffers severely from sulphur content. Heavy fuels may have high concentrations of sulphur, which may make reforming economically unattractive. Sulphur is a very severe poison, especially in the case of nickel catalysts. In reformers, sulphur accumulates at the inlet meaning that unconverted higher hydrocarbons may pass to the hotter part, where coking is more critical and steam cracking may occur. (Rostrup-Nielsen, Tottrup, 1979) Problems in obtaining satisfactory desulphurisation have resulted in accepting the poisoning of the nickel surface in commercial processes, leaving steam cracking as the dominating reaction path. In such a case the exit gas contains higher hydrocarbons such as ethylene and propylene. (Rostrup-Nielsen, Tottrup, 1979) Another possibility is to use a nickel free catalyst.

Nevertheless, Haldor Topsøe have recently published the successful development of a combined hydrodesulphurisation and pre-reforming system for logistic fuels in fuel cell applications. (Piwetz, Larsen & Christensen, 1996; Rostrup-Nielsen, Christensen & Dybkjaer, 1998) In a study for the US Military, Haldor Topsøe conducted laboratory tests and subsequent scale-up of hydrodesulphurisation and adiabatic pre-reforming of diesel (DF-2) and jet fuel (JP-8). Using Haldor Topsøe's RKNR catalyst (cf. Table 1.1), a series of laboratory tests were conducted with a total of 1,900 hours (diesel) and 500 hours (jet fuel). Properly designed, the combined hydrodesulphurisation and adiabatic pre-reforming process reached full conversion of either fuel without higher hydrocarbons or sulphur in the outlet.

A pilot plant adiabatic pre-reformer with RKNR catalyst was constructed and a 1,000 hours test on diesel and 500 hours on jet fuel was conducted. (Piwetz, Larsen & Christensen, 1996) Temperature profiles are shown in Figure 1.2. Sufficiently stable operation was obtainable, with the required size of the catalyst bed determined by poisons in the feed stream, mainly sulphur. In case of diesel feed, some gum formation was also observed. At the same space velocity, a longer lifetime is achieved with jet fuel because the deactivation rate is lower and reaction rates are higher. However, a fuel processing system for both diesel and jet fuel can be designed and operated satisfactorily. Further scale-up was done to a 32kW fuel processor including hydrodesulphurisation and adiabatic pre-reforming. Tests were conducted for over 1,900 hours with commercial diesel (360 ppmw S in, 1 ppmw of sulphur in the pre-reformer feed). A total of 5.75 kg/hr of diesel was processed with no significant difficulties reported.



Feed:	IBP /°C	FBP /°C	Aromatics (wt.%)	Sulfur ^a (wt. ppm)
Jet fuel	137	262	19	0.7
Diesel	132	368	26	1.0

^a Inlet pre-reformer.

Conditions: $H_2O/C = 2.4$, $H_2/C_nH_m = 0.5 \text{ Nm}^3 \text{ kg}^{-1}$, $P = 25 \text{ bar}$.

Figure 1.2 Temperature profiles during adiabatic pre-reforming of jet fuel and diesel by Haldor Topsøe over RKNGR catalyst (Rostrup-Nielsen, 2001)

1.2.2 Reaction with Steam

Phillips et al. (1970) tested the reaction of n-heptane with steam over a 75%Ni/alumina catalyst between 350°C and 500°C. At different values of the conversion (that were achieved by either feed flow variation or by catalyst deactivation) the product composition appeared to be a function of the feedstock conversion only. Initial products were found to be hydrogen and carbon oxides and later methane was produced. Direct formation of methane from hydrocarbon and steam is excluded, based on the fact that methane is observed below its equilibrium value while hydrogen and carbon oxides in excess of the methanation/steam reforming equilibrium.

More recently, Arena et al (2004; 2006) found similar trends when studying pre-reforming of n-hexane over 19.1 % (w/w) NiO/MgO at 450°C and 10-15 bar. The only product was C_1 components, except when hydrogen was fed at $H_2/C=1$ and traces of C_2-C_5 were observed. At conversions above 50%, the selectivity for methane and carbon dioxide were 55–60% and 45%, respectively. At 10% conversion the main product was CO_x , indicating that methane is a secondary product formed from carbon oxides.

1.2.3 Additional Reactants

Stability of the pre-reforming process for heavy hydrocarbon feedstock may be enhanced by the addition of other reactants besides steam.

Addition of hydrogen to the feed improves the stability of adiabatic pre-reformers. High hydrogen to carbon ratio is known to retard the formation of polymeric deposits. (Kikuchi, Ito & Morita, 1975; Davies, Templeman & Wragg, 1975; Christensen, 1996; Sperle, 2005) (Cf. Section 4.2) As mentioned in the previous section, there is some evidence that hydrogen may produce higher hydrocarbons at low temperature in specific conditions. (Arena, 2004; Arena, 2006)

While the addition of hydrogen can be very effective in reducing coke deposition, it does increase the adiabatic temperature rise by affecting the methanation equilibrium. (Davies, Templeman & Wragg, 1975) In this respect, recycling of reformat is another option for effectively decreasing coke deposition. (Rostrup-Nielsen, Tottrup, 1979)

Somewhat more exotically, the incorporation of $ZrOCl_2$ into the substrate of steam reforming catalysts effectively reduces both the sulphur poisoning as well as the coke deposition (Andersen, 1986). However, a small partial pressure of chlorine must be present during the reaction and this is not a feasible option for fuel processing applications for fuel cell systems.

1.2.4 Parallel Reactions and By-Products

A well designed process will allow complete conversion of the feedstock into C_1 components, without the involvement of intermediates. The only possible exception is benzene, which has been observed by Rostrup-Nielsen (1973) over a nickel catalyst and by several authors using precious metal catalysts. (Kikuchi, Ito & Morita, 1975; Springmann, 2002; Wang, Gorte, 2002) However, at elevated temperatures, by-products may be formed. Pyrolysis normally becomes significant above 920K, however an acidic material may promote cracking reactions at temperatures as low as 870K. (Rostrup-Nielsen, 1984) Several experimental studies observe the formation of C_1+ hydrocarbons at elevated temperatures. Haji, Ziemlewski and Erkey (2003) studied steam reforming at 500–1000K of n-hexadecane over supported Pt, Rh, and Pd catalysts. Ethane and ethylene by-products were found at the higher temperatures. Similar findings are reported by Springmann et al. (2002), who studied steam reforming of iso-octane and toluene over a proprietary noble metal catalyst by OMG at 600 – 700°C. Ethane and ethylene were observed for the reforming of iso-octane, while steam reforming of toluene was found to proceed via dealkylation to benzene. Benzene is probably converted into carbon monoxide directly, as no other intermediates were detected.

1.2.5 Thermodynamics

The reactions scheme presented in Section 1.2.2 can be made explicit for 1-tetradecene according to (thermodynamic data from Roine, 2002):



The values of the equilibrium constants of the three reactions are shown versus temperature in Figure 1.3. The equilibrium constant for the steam reforming of 1-tetradecene is unity around 375°C and above that temperature the equilibrium is heavily shifted towards the product side. In case carbon monoxide is the only reaction product, the steam reforming of higher hydrocarbons must be considered an equilibrium reaction. (Ross, 1975) However, this may change in case water-gas shift and methanation affect the equilibrium. Indeed, even at the lowest temperatures relevant for pre-reforming, the steam reforming reaction must be considered irreversible as the equilibriums of water-gas shift and methanation are established very fast. (Rostrup-Nielsen, 1984) This is further sustained by experimental findings that suggest no higher hydrocarbons are produced from carbon monoxide and hydrogen. (Christensen, 1996)

The equilibriums for water-gas shift and methanation (Figure 1.3) both lie to the product side at pre-reforming temperatures ($T < 600^\circ\text{C}$) and the pre-reformer product at equilibrium is to be expected rich in methane and carbon dioxide. This is shown in Figure 1.4, expressed by gas phase composition at thermodynamic equilibrium: below 500°C carbon is almost completely converted into CO_2 and CH_4 .

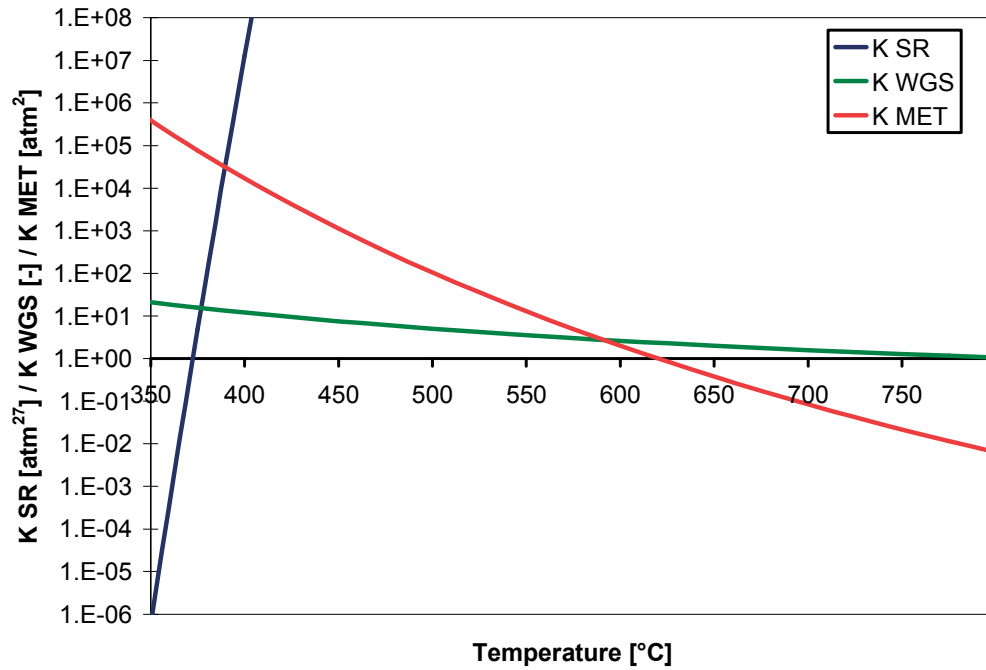


Figure 1.3 *Equilibrium constants for steam reforming of 1-tetradecene, water-gas shift, and methanation reactions 350–1000°C (Roine, 2002)*

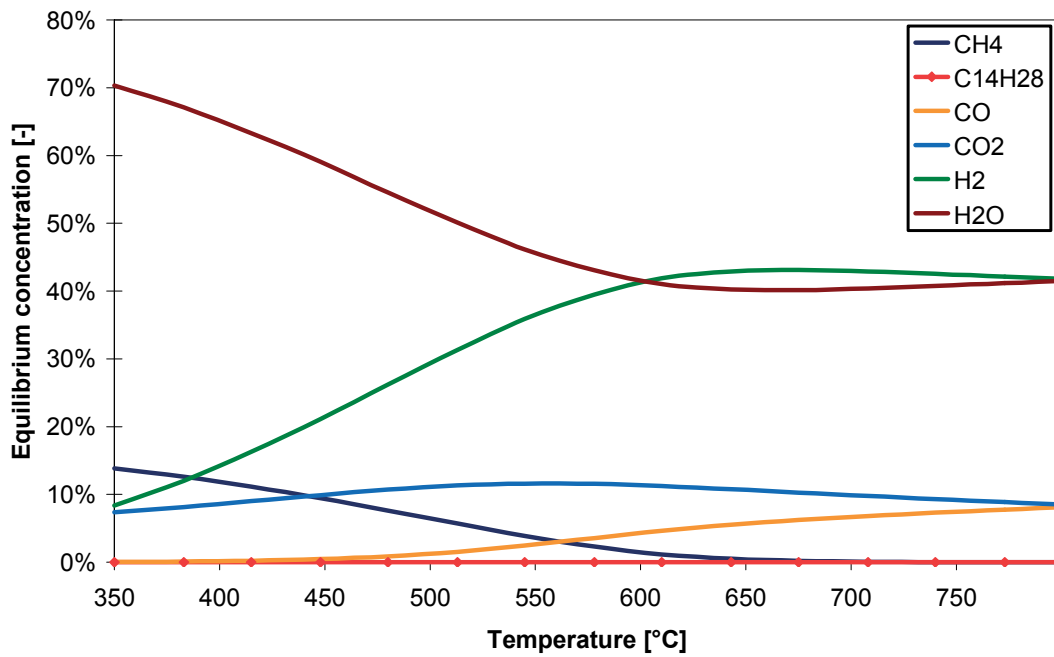


Figure 1.4 *Equilibrium composition versus temperature, starting from 1 mole of C₁₄H₂₈ and 56 moles of H₂O (S/C = 4) at 1 bar total pressure (Roine, 2002)*

2. Pre-reforming Catalysts

Group VIII metals are catalytically active for the steam reforming reaction. Nickel is the active metal in almost all industrial catalysts. Iron will be oxidised and cobalt is hardly stable in metallic state at typical $\text{H}_2\text{O}/\text{H}_2$ ratios. (Rostrup-Nielsen, 1984) Precious metals are very active for the steam reforming as well. Sometimes precious metals are considered to be too expensive for general commercial use (Rostrup-Nielsen, 1984), but this may change with the processing of heavier feedstock and/or the recycling of precious metals. (Hagelüken, Verhelst, 2004)

The application of nickel catalysts at the relatively low pre-reforming temperature calls for a high surface area in order to obtain sufficient activity. During the process the activity is further impeded by degradation, most notably by coke deposition and sulphur poisoning. While the sulphur resistance of catalysts remains problematic, the resistance to coke formation can be improved by promotion of the nickel catalyst, or by making use of noble metals.

2.1 Nickel-based Catalysts

2.1.1 Active metal

Nickel crystals are the active phase for catalysing hydrocarbon reforming reactions. Metallic nickel is stable with 0.3–0.6 % (v/v) of hydrogen in steam. However, support interactions and crystal size effects may decrease the free energy of nickel oxide and in practice reduced catalysts will be oxidised when exposed to steam containing 2–10 % (v/v) hydrogen (i.e., $p_{\text{H}_2\text{O}}/p_{\text{H}_2} = 10\text{--}50$), or to mixtures with an equivalent oxidation potential. Reduction of NiO by hydrogen starts at temperatures 470–520 K, yet the reduction of supported catalysts requires higher temperatures due to interaction with the support. (Rostrup-Nielsen, 1984)

Industrial activation is usually carried out by means of the feed stream, consisting of steam and hydrocarbons at a high steam-to-carbon ratio (5–10) and low pressure. (Rostrup-Nielsen, 1984) The hydrocarbons crack thermally and the hydrogen and carbon products act as initiators of the reduction process. As soon as metallic nickel is available, steam reforming will provide sufficient hydrogen for quick reduction of the catalyst. Similarly, addition of small amounts of hydrogen to the feed enhances the initial reduction. The temperature of 'ignition' depends on the reactivity of the hydrocarbon and on the catalyst. In fact, when operating with pure methane (e.g. laboratory reactors), the $p_{\text{H}_2\text{O}}/p_{\text{H}_2}$ value at the reactor inlet may even be high enough to oxidise the catalyst and additional hydrogen must be supplied during the process.

The activated catalyst consists of nickel crystallites on the catalyst support. Both the activation procedure and the operating conditions influence the size of the nickel surface. At elevated temperatures, nickel crystals may sinter and lose surface area. Corresponding to the rule of Tamman, sintering is observed above $\frac{1}{2}T_m$ of the metal, which is 864 K for nickel. Surface diffusion may start above the Hüttig temperature, or 576 K, and result in reorganisation of the Ni crystals. Unfortunately, the sintering mechanism is not yet completely understood. However, metal particles cannot grow to a size larger than the pore diameter, so a stabilised micropore system may prevent excessive sintering of the nickel crystals. (Rostrup-Nielsen, 1984)

2.1.2 Support

Mechanical properties of the catalyst are critical. The material for catalyst support is mainly restricted by temperatures and steam partial pressures. Industrial steam reforming catalysts are based on ceramic oxides or oxides stabilised by hydraulic cement. Typical ceramic supports are α -alumina, magnesia, magnesium aluminium spinel, and zirconia fired above 1270K. Cement-type catalysts are normally stabilised by a silica-free binder such as calcium aluminate.

(Rostrup-Nielsen, 1984) For pre-reforming processes the requirements are somewhat less severe and the emphasis shifts to high surface area supports, such as γ -alumina, chromia, etc. (Rostrup-Nielsen, 1984)

Substantial sintering and weakening of the support is encountered at temperatures above 770K. (Rostrup-Nielsen, 1984) The deterioration is strongly accelerated by the high steam partial pressure and stability tests at atmospheric pressure can be misleading. Magnesia may be added to the catalyst support for enhanced steam adsorption, but this may deteriorate steam tolerance. While it is resistant to high temperature steam, magnesia suffers from steam at lower temperatures due to hydration: (Rostrup-Nielsen, 1984)

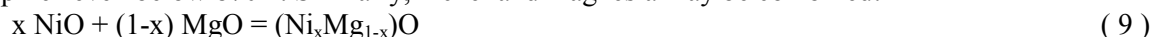


Expansion of the molecular volume may result in breakdown of the catalyst. Fortunately, the reaction takes place in liquid water and the formation of hydrates is only a problem when operating close to the dew point of water, or when the catalyst is (incidentally) exposed to liquid water.

In operation, active nickel crystallites may interact with the support, forming inactive mixed metal oxides. (Rostrup-Nielsen, 1984) For example, nickel supported on alumina forms a spinel structure:



Nickel spinel is formed above about 970K. However, it is possible to form an inactive 'surface spinel' even below 870K. Similarly, nickel and magnesia may be combined:



Again, less well crystallised structures have been observed at low temperature and low hydrogen partial pressure. These may keep nickel in the oxidised rather than in the active metallic state.

2.1.3 Additives

A great number of oxides have been proposed as promoters for nickel catalysts, either to improve activity or to reduce the formation of coke.

Formation of coke is depressed by enhanced steam adsorption on the catalyst, which can be achieved by the presence of alkali or by the use of magnesia based catalyst. (Rostrup-Nielsen, 1975) Already in the late 1960s, the increased coking resistance obtained by alkali, specifically potassium, was recognised. ICI claimed a liquid hydrocarbon reforming catalyst with reduced coking, based on the addition of alkaline earth metal oxide (typically CaO) and alkali metal oxide (typically K_2O). They were able to reform naphtha at temperatures in the range of 400 – 750°C (Chinchen, Schnell, 1971) Alkali is thought to decrease carbon deposition by preferentially binding to step edges of the nickel crystals, that are very active for carbon deposition. (Bengaard, 2002; Shekawat, 2006) However, by binding to active sites the addition of alkali implies a significant drop in catalytic activity. (Rostrup-Nielsen, 1973)

Phillips Gasolineum patented nickel catalysts for higher hydrocarbon steam reforming and pre-reforming, supported on calcium phosphate or alumina and promoted with barium and/or uranium. (Pitchford, Walker & Johnson, 1971; Johnson, Nowack, 1977)

The incorporation of ZrOCl_2 into the substrate of steam reforming catalysts effectively reduces both the sulphur poisoning as well as the coke deposition (Andersen, 1986). However, a small partial pressure of chlorine must be present during the reaction and this will present a problem in pre-reforming processes in general.

At the National Institute of Advanced Science (AIST) in Tsukuba, Japan, a series of Ni-Re-based catalyst has been tested for the fuel processing of liquid hydrocarbons, mainly with methylcyclohexane (MCH). The catalyst however appears to be directed to elevated temperatures:

803K for MCH to 953K for gasoline. (Murata, 2004; Wang, Murata& Inaba, 2004a; Wang, Murata& Inaba, 2004b; Wang, Murata& Inaba, 2005; Wang, Murata& Inaba, 2006)

The addition of partially reducible and oxygen conducting oxides to reforming catalysts is often claimed to induce a higher activity and greater stability. (Shekawat, 2006) Probably, the primary role of ceria is the ability to dissociate water and transfer the oxygen to the supported metal. Consequently ceria may be able to maintain the surface relatively free from carbon. (Wang, Gorte, 2002) In the seventies Tokyo Gas already suggested lanthanum oxide (La_2O_3) and ceria (CeO_2) to improve standard nickel-alumina reforming catalysts, specifically for higher hydrocarbons ($\text{C}_2\text{--C}_{12}$). (Anon., 1978) Bhat and Bhat (2005) suggest the use of partially reducible oxides and lanthanum oxide in group VIII metal catalysts for higher activity, a better sulphur tolerance and an increased resistance to coking during diesel steam reforming. An increased sulphur tolerance and coking resistance by using a mixed oxygen ion and electron conducting material is claimed by Cable et al. (2001) in steam reforming of diesel and ($360^\circ\text{C} - 1000^\circ\text{C}$, $\text{S/C} = 3.8\text{--}4.7$). Recently, an experimental programme at the Dalian Institute of Chemical Physics resulted in the successful pre-reforming of simulated gasoline (74% iso-octane, 20% xylene, 5% cyclo-hexane, and 1% 1-octene at 480°C and 5 bar) over a catalyst consisting of NiO and La_2O_3 supported on alumina for 100 hours. (Chen, 2006a; Chen, 2006b; Yu, 2006; Chen, 2007) In another study, an adiabatic pre-reformer was placed upstream of an autothermal reformer, based on a NiO / MgO / La_2O_3 catalyst. (Chen, 2006b)

The addition of metals to the nickel has been proposed in order to reduce the formation of carbon filaments. Carbon whiskers are formed via the formation of nickel carbide and the diffusion of carbon through the nickel crystallites (cf Section 4.2.3). The addition of another metal to nickel may effectively prevent this mechanism. Trimm (1997b) suggests that silver reacts with the orbitals of nickel used in carbide formation. His experiments with methane reforming show that the formation of carbon is reduced significantly upon the addition of 0.25% silver, albeit at the expense of a slightly lower activity. Gold, like alkali, preferentially binds to the step edges of nickel that are most active in carbon formation. (Shekawat, 2006) Bartholomew (2001) mentions a 16%Ni/MgAl₂O₄ catalyst promoted with 0.3% Au to be stable for over 4,000 hours in steam reforming of n-butane.

2.2 Precious Metal Catalysts

Whereas nickel-based catalysts are very vulnerable to coke deposition, precious metal catalysts have been proposed as viable alternatives, for example in the field of fuel processing. The tendency for the formation of carbon whiskers may be practically eliminated by the use of a platinum, ruthenium, or rhodium catalyst as will be explained in Section 4.2.3. In addition, the sensitivity for sulphur poisoning may be less than for nickel catalysts.

Rostrup-Nielsen (1984, Table 11) collected literature data for turnover frequencies in the steam reforming of methane, ethane, and toluene. For toluene the relative turnover frequencies may be ranked as: Rh (11) > Ru (6) > Pd (4) > Pt (2) > Ir (2) > Ni (1), so many alternatives to nickel may be considered and are in fact encountered in literature. Zheng, Strohm and Song (2003) performed experiments of pre-reforming jet-fuel (NORPAR-13, mainly normal paraffin with average size C_{13}). With 4 ppmw of S, $\text{S/C} = 3$, atmospheric pressure. Around 500°C , the catalytic activity of metals was ranked as: Rh ~ Ru > Ir > Pd ~ Pt > Ni. The optimum catalyst, however, seems to depend not only on the turnover frequency of the metal, but also on process conditions, feedstock, and additives.

Engelhard Industries (Pfefferle, 1969) have claimed a process for the steam reforming of naphtha in two stages, the first of which is to be operated at an inlet temperature below 550°C and a maximum temperature below 650°C . The catalyst is based on a platinum group metal and hydrogen is added to the feed in order to improve catalyst stability. The catalyst is claimed to be sulphur tolerant up to 100 ppm. The patent reports a test of steam reforming JP4 fuel with 24%

of aromatics with 33 ppm of sulphur at a WHSV of $1 \text{ m}^3 \cdot \text{kg}^{-1} \cdot \text{hr}^{-1}$ over a catalyst containing 0.4% (w/w) platinum and 0.1% (w/w) rhodium on alumina.

Delahay, Bousquet and Duprez (1985) compare steam reforming of methyl-1-naphthalene at 440°C on alumina-supported Rh, Ni, and Pt. The mechanistic results are treated in Section 3.2, but in summary, the relative activity of the active metals is ranked as $\text{Rh} \gg \text{Ni} > \text{Pt}$. Platinum is very selective for dealkylation while only nickel and rhodium appear to be effectively able to open aromatic rings. The activity of rhodium catalysts appears to be support sensitive, in contrast with nickel, since $\text{Rh}/\text{Al}_2\text{O}_3$ is significantly more active than Rh/SiO_2 .

Thormann et al. (2008) studied steam reforming of iso-octane and hexadecane over a 21% (w/w) $\text{Rh}/\text{Al}_2\text{O}_3$ catalyst in a microreactor. With hexadecane, rapid deactivation was observed over a period of 12 hours, which has been attributed to soot formation. The catalyst activity could be readily restored in air at 750°C . The reaction products with hexadecane contained CO , CO_2 , H_2 , and CH_4 , as well as 300 ppmv C_2H_6 , 200 ppmv of $\text{C}_{16}\text{H}_{34}$ and traces of pentane, hexane, and decane. As little by-products were observed the role of homogeneous gas-phase reactions in the process can be neglected.

Precious metals, like nickel, may benefit from the addition of partially reducible oxides in terms of resistance to coking and tolerance towards sulphur. Unfortunately, most experimental evidence seems to be directed at direct steam reforming at elevated temperatures rather than at pre-reforming conditions. Nevertheless, the results may be illustrative. Suzuki, Iwanami, and Yoshinari (2000) were able to improve the sulphur tolerance of a ruthenium steam reforming catalyst by addition of ceria and perform direct steam reforming of hydrodesulphurised kerosene for 8,000 hours. Ando et al. studied steam reforming of dodecane (both in presence and absence of oxygen) over rhodium, ruthenium, and iridium supported on lanthanum oxide (La_2O_3) at 773–1073K. In the absence of oxygen, rhodium and ruthenium were superior. (Ando, 2002) InnovaTek claims to have developed a proprietary catalyst for the steam reforming of liquid fuels, with enhanced resistance to coking and sulphur poisoning. The catalyst, called ITC, consists of a bimetallic compound supported on a high surface area alumina, treated with an oxygen ion conductor for improved stability. (Ming, 2002) The addition of ceria also affects the water-gas shift activity as Wang and Gorte (2002) showed that $\text{Pd}/\text{alumina}$ is a much poorer shift catalyst than Pd/ceria . The reduction of coke deposition by ceria was also shown by Zheng, Strohm and Song (2003) by performing experiments of pre-reforming jet-fuel (NORPAR-13, mainly normal paraffin with average size C_{13}). With 4 ppmw of S, $\text{S}/\text{C} = 3$, atmospheric pressure and at 514°C , $\text{Rh}/\text{Al}_2\text{O}_3$ with and without CeO_2 were tested. The effect of CeO_2 on carbon formation was shown by TPO-IR studies of spent catalysts after 10 hours of pre-reforming. Both samples show peaks originating from CO_2 desorption and the oxidation of amorphous carbon. In contrast, peaks at higher temperatures that are indicative of filamentous carbon were absent in the sample containing CeO_2 . Haji, Ziemlewski and Erkey (2003) have tested both commercially available Pt, Rh, and Pd based catalysts (all 0.5% (w/w) on Al_2O_3) and synthesised 1% (w/w) Pt/CeZrO_x for steam reforming of n-hexadecane at steam to carbon ratios of 1 and 2, and temperatures of 500–1000K. The higher temperatures resulted in the formation of ethane and ethylene by-products, which is to be expected if ethane and ethylene are formed via the (steam) cracking route as explained in Section 1.2.4. Without reporting explicit experimental results, the authors claim that platinum supported on ceria-zirconia is more active than platinum supported on alumina. Shekawat et al. (2006) mention the use of ruthenium based catalysts as well as ceria supported platinum and palladium for steam reforming of higher hydrocarbons. Acharya, Lane and Krause (2006) performed a kinetic study of i-butane steam reforming over platinum supported on cerium-gadolinium oxide (CGO).

A promising development in terms of sulphur tolerance has recently been put forward by Lu et al. (Lu, 2008). Iso-octane with 300 and 500 ppmw of sulphur was reformed over a 1.5% (w/w) $\text{Pt}/\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (PtCGO) catalyst, with $\text{S}/\text{C}=3$ at 750°C and for up to 100 hours. In comparison, 1.5% (w/w) $\text{Pt}/\text{Al}_2\text{O}_3$ and 10% (w/w) $\text{Ni}/\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ showed rapid sulphur poisoning.

The sulphur was present as thiophene while the reactor outlet solely contained H₂S. The conversion of thiophene to H₂S is believed to proceed via a redox mechanism, in which the reducibility of the CGO support plays a role. An optimum was found for the calcination temperature of the PtCGO catalyst: the sample calcined at 800°C performed better than the samples calcined at either 600°C or 1000°C. Consequently, metal-support interactions between the platinum and the fluorite are assumed to be the cause of catalyst stability and the enhanced sulphur tolerance.

Just as nickel catalysts potentially benefit from the addition of precious metals (cf. Section 2.1.3), precious metals may benefit from the addition of base metals. Fukunaga et al. of Idemitsu Kosan, Tokyo, (Fukunaga, 2003; Fukunaga, 2004) have developed reforming catalysts based on ruthenium, in combination with additives such as cobalt, magnesium, and manganese. The catalysts have been tested both for direct steam reforming and for pre-reforming of desulphurised kerosene (S < 0.05 ppm). The patent describes a preferential operating temperature of 300 – 600°C, LHSV of 0.25-5 hr⁻¹ (GHSV ~ 250-5,000 hr⁻¹), and S/C = 2-4. Operating above 600°C leads to carbon formation by thermal cracking reactions. Strohm, Zheng, and Song (2006) extensively investigated sulphur tolerance in pre-reforming of jet fuel over rhodium and rhodium-nickel catalysts (< 520°C). Monometallic Rh/CeO₂-Al₂O₃ catalysts suffered from sulphur poisoning during reforming of feedstock with > 10 ppmw of sulphur. Especially the methanation activity rapidly deteriorates in presence of sulphur. Addition of nickel to the rhodium catalyst leads to an increased sulphur tolerance: nickel acts as protective and even sacrificial metal. Bimetallic Rh-Ni/CeO₂-Al₂O₃ catalyst allows for successful pre-reforming of JP-8 jet fuel with 22 ppm of sulphur for up to 72 hours.

2.3 Other Catalysts

Very little data is available on catalysts not based on group VIII metals and the results are rather poor.

Mitsubishi Chemical Industries have patented naphtha reforming catalysts based on vanadium or molybdenum. (Arakawa, Oka, 1974)

Problems with sulphur resistance have led to the development of non-metallic catalysts for steam reforming of hydrocarbons. The results, however, have been rather disappointing. Due to low activities, the process must be carried out at elevated temperatures. Because of the higher temperatures, steam cracking will take place entailing high rates of coke deposition. (Rostrup-Nielsen, 1984)

3. Diesel Pre-reforming Kinetics and Mechanism

As explained in more detail in Section 1.2, the pre-reforming process is based on three main reactions: steam reforming, water-gas shift and methanation (cf p. 10). In any practical reactor, the latter two will be at or close to thermodynamic equilibrium, while the former is irreversible and no gas-phase intermediates are normally observed. (Section 1.2.5) Therefore, kinetics of the pre-reforming reactions reduces to kinetics of the steam reforming reaction at relevant conditions. Kinetics of steam reforming is known to differ substantially for different catalysts. (Rostrup-Nielsen, 1973) Below, literature on relevant kinetics is treated in two separate sections, one for nickel-based catalysts and one for precious metals.

3.1 Base Metal Kinetics and Mechanism

A simplified model (Rostrup-Nielsen, Tottrup, 1979) of steam reforming at 400-600°C includes irreversible adsorption of the hydrocarbon on the nickel surface. The hydrocarbon subsequently leaves the surface as C₁ molecules, or stays as carbon. This is supported by the fact that no intermediates are generally found at temperatures below 600°C. (Rostrup-Nielsen, 1973; Rostrup-Nielsen, Tottrup, 1979) Perhaps the only exception is benzene, which has been observed as a reaction product by Rostrup-Nielsen in the reforming of naphtha over a nickel catalyst. (Rostrup-Nielsen, 1973) At higher temperatures, the reaction on the nickel surface may be accompanied by thermal cracking (or cracking on the support) of the hydrocarbon, resulting in olefins as intermediates. Reforming reactions may therefore change gradually into steam cracking reactions and as a result hydrogenated products (ethane, propane etc) may be found in the reformer effluent at elevated temperatures. Kinetics of the water-gas shift and methanation reactions appear to be very fast, compared to the reforming kinetics.

Kinetics and specific activity for reforming reactions vary significantly from catalyst to catalyst. (Rostrup-Nielsen, 1973) Major differences are in the influence of steam partial pressure, related to the ability of the carrier to adsorb steam. Active magnesia and alkali, for example, enhance steam adsorption. The specific activity of nickel for reforming, hydrogenolysis, and methanation is also strongly influenced by the carrier employed and the presence of alkali. However, addition of alkali entails a significant drop in specific activity, the effect of potassium being larger than for sodium.

Kinetics cannot be described by a simple power law in a broad temperature range because the powers vary with temperature. (Rostrup-Nielsen, 1973) Reactivity of n-paraffins at equal partial pressure appears to increase with the number of carbon atoms. The reactivity of branched hydrocarbons and cycloparaffins appears higher than those of n-paraffins, whereas aromatics show poor reactivity.

Based on a large body of experimental findings, it may be safely concluded that the reforming of higher hydrocarbons at low temperature does not proceed via hydrocarbon intermediates. Analyses of higher hydrocarbons in low temperature reformer product gas show compositions very close to the feedstock, with a notable exception for benzene. (Rostrup-Nielsen, 1984) At low temperatures (< 840K) no hydrocarbons other than methane were found among the products, also at low conversions. Some authors report formation of lower olefins at elevated temperatures (e.g., 870K) but this seems to be caused by thermal pyrolysis or cracking on the support rather than from reaction intermediates. At any case the role of olefins as intermediates up to 770K can be excluded. (Rostrup-Nielsen, 1984)

Arena et al (2004; 2006) studied pre-reforming of n-hexane over 19.1% (w/w) NiO/MgO at 450°C and 10–15 bar. In contrast with findings by others, traces of C₂–C₅ were observed when hydrogen was fed at H₂/C=1, but otherwise the only products were C₁ components. The selec-

tivity for methane and carbon dioxide changed from 55–60% and 45% at high conversion (> 50%), to mainly CO_x at low conversion (10%). The results were explained by two mechanisms: steam reforming and steam cracking. (Figure 3.1) In the steam reforming reaction, n-hexane is converted into carbon monoxide, which is subsequently converted into carbon/methane on the one and into carbon dioxide on the other. The steam cracking reaction involves the direct formation of coke from n-hexane, followed by conversion to either carbon oxides or methane.

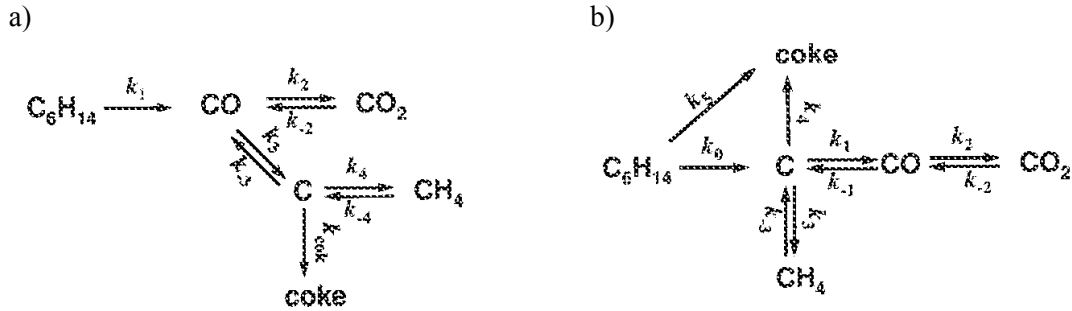


Figure 3.1 Steam reforming (a) and cracking (b) mechanisms proposed by Arena et al (2004; 2006)

Over a limited range of process conditions, the rate equation may be simplified to a power law equation:

$$r = k_{\infty} e^{-\frac{E_a}{RT}} p_{C_nH_m}^{\alpha_{C_nH_m}} p_{H_2O}^{\alpha_{H_2O}} p_{H_2}^{\alpha_{H_2}} \quad (10)$$

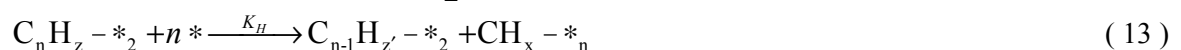
Rostrup-Nielsen (1984) has collected kinetic data for the steam reforming of methane through n-heptane and observed that $\alpha_{C_nH_m}$ tends to approach zero as k_{∞} increases. Similarly, the retarding effect of aromatics can be explained in terms of a high affinity for adsorption and hence a large value of k_{∞} . The reaction order with respect to steam appears to vary between -0.6 and 1 depending on operating conditions and catalyst. The order with respect to hydrogen varies in a rather complex manner.

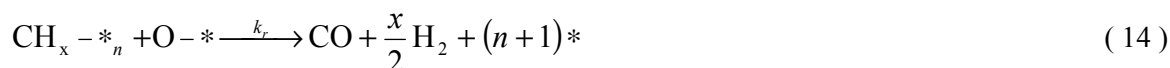
Praharso et al. (Praharso, 2004) performed a kinetic study at 583-623K of steam reforming of iso-octane over a commercial alumina-supported Ni catalyst. Remarkably, small amounts of acetylene were detected, but this is not discussed by the authors. The fitted rate equation (pressure in kPa) amounts to:

$$r = 0.0026 e^{-\frac{44.0 \text{ kJ/mol}}{RT}} p_{i-C_8H_{18}}^{0.17} p_{H_2O}^{0.54} \left[\frac{\text{mol}}{\text{g} \cdot \text{s}} \right] \quad (11)$$

As the reaction order is 0.2 with respect to iso-octane, strong hydrocarbon adsorption apparently leads to high surface coverage by hydrocarbons. Mechanistically, the reaction was successfully fitted to a Langmuir-Hinshelwood mechanism with dissociative adsorption of iso-octane and steam on two different sites. Rate determining step appears to be the reaction of dissociatively adsorbed species of iso-octane and steam.

It is assumed that, around 500°C, the hydrocarbon is chemisorbed on a dual site followed by successive α -scission of the C-C bonds. (Rostrup-Nielsen, 1973; Rostrup-Nielsen, 1984) The resulting C₁-species react with adsorbed steam on the nickel surface. Accordingly, a mechanism has been proposed: (Rostrup-Nielsen, 1984; Rostrup-Nielsen, Christensen & Dybkjaer, 1998)





If the concentration of $\text{C}_n\text{H}_z - *_2$ is negligible and Langmuir adsorption applies, the following rate equation may be obtained: (Rostrup-Nielsen, 1973; Rostrup-Nielsen, 1977)

$$r = \frac{k_A \rho_{\text{C}_n\text{H}_m}}{\left(1 + \frac{nk_A}{k_r K_W} \frac{\rho_{\text{H}_2}}{\rho_{\text{H}_2\text{O}}} \rho_{\text{C}_n\text{H}_m} + K_W \frac{\rho_{\text{H}_2\text{O}}}{\rho_{\text{H}_2}} + \sqrt{K_H \rho_{\text{H}_2}} \right)^2} \quad (17)$$

Using a 22 % (w/w) nickel on magnesia catalyst, Tøttrup (1982) measured kinetic data for n-heptane pre-reforming under diffusion limitation. Conditions were varied between 450–550°C and 5–30 bar, around S/C = 4, and $\text{H}_2\text{O}/\text{H}_2 = 20$. Sulphur content of the feed was below 0.05ppm (w/w). By back-calculation with an effective diffusion coefficient for n-heptane, intrinsic kinetics was determined (with pressure in bar) according to:

$$r = \frac{8 \cdot 10^5 e^{\frac{-67.8 \text{ kJ/mol}}{RT}} \rho_{\text{n-C}_7\text{H}_{16}}}{\left(1 + 25.2 \rho_{\text{n-C}_7\text{H}_{16}} \frac{\rho_{\text{H}_2}}{\rho_{\text{H}_2\text{O}}} + 0.077 \frac{\rho_{\text{H}_2\text{O}}}{\rho_{\text{H}_2}} \right)^2} \quad \left[\frac{\text{mol}}{\text{g} \cdot \text{h}} \right] \quad (18)$$

3.2 Precious Metal Kinetics and Mechanism

At Waseda University, Tokyo, the reactivity of several hydrocarbons has been evaluated in steam reforming of a 1% (w/w) rhodium on alumina catalyst at 500–600°C. (Kikuchi, Ito & Morita, 1975) The reactivity of the components has been ranked as: n-pentane \approx benzene \geq 2,2,4-trimethylpentane > n-heptane > toluene. Based on measurements with all components, the mechanism for steam reforming n-heptane proposed is depicted in Figure 3.2. It is suggested that the reactivity of n-heptane and toluene is relatively low because their gasification takes place via adsorbed cyclic intermediates, and adsorbed benzene, respectively. Toluene was found to be hardly decomposed directly, but rather through slow demethylation to benzene, of which gasification is fast. N-pentane and 2,2,4-trimethylpentane, on the other hand, react relatively fast since no cyclic intermediates are formed. The direct route for steam reforming of n-heptane irreversible: no paraffin hydrocarbon by-products are observed. The direct route for n-heptane steam reforming is the main reaction path at 500°C while the route via aromatics prevails at higher temperature (600°C). However, the aromatics rapidly decompose at 600°C and are only observed at small contact times.

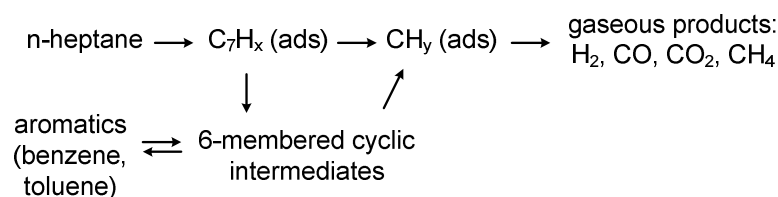
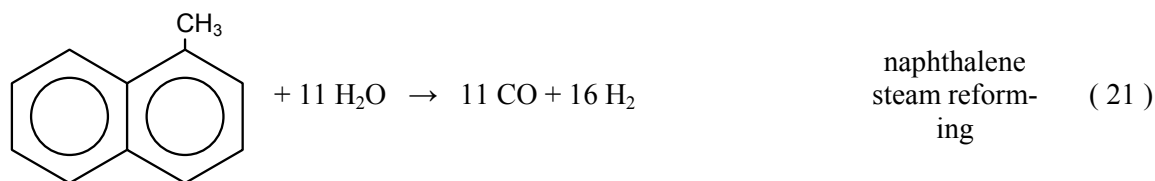
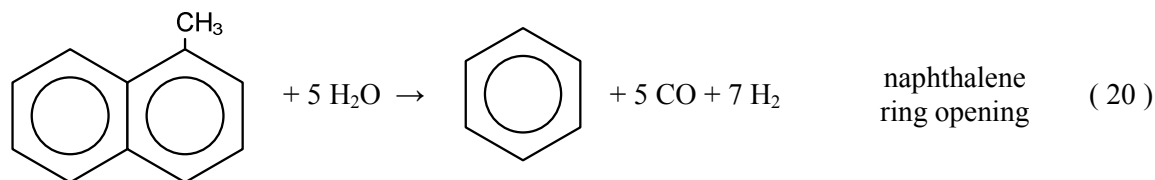
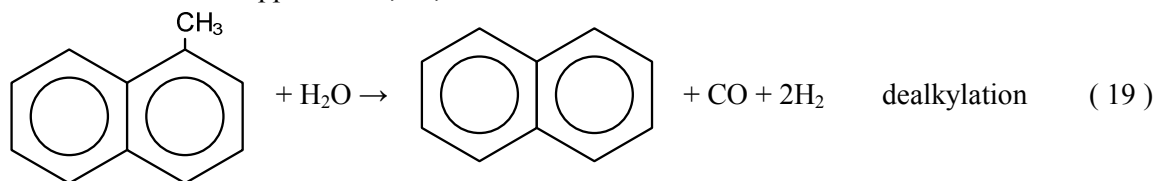


Figure 3.2 Proposed mechanism of steam reforming of n-heptane over rhodium-based catalyst at 500–600°C (Kikuchi, Ito & Morita, 1975)

Delahay, Bousquet and Duprez (1985) compare steam reforming of methyl-1-naphthalene at 440°C on alumina-supported Rh, Ni, and Pt. Three reactions are observed:

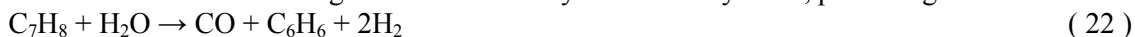


The relative activity, based on the total amount of methyl-1-naphthalene converted, of the active metals is ranked as Rh >> Ni > Pt. The initial selectivity (no deactivation data is reported) of methyl-1-naphthalene is ranked as:

- Platinum: 84% to naphthalene (19), 11% to benzene (20), and 5% to CO (21),
- Rhodium: 55% to naphthalene (19), 30% to benzene (20), and 14% to CO (21),
- Nickel: 36% to naphthalene (19), 29% to benzene (20), and 35% to CO (21).

Clearly platinum is very selective for dealkylation. Only nickel and rhodium appear to be effectively able to open aromatic rings. In addition, the activity of rhodium catalysts appears to be support sensitive, in contrast with nickel, since Rh/Al₂O₃ is significantly more active than Rh/SiO₂.

The dealkylation route is further supported by Springmann et al. (2002), who studied steam reforming of iso-octane and toluene over a proprietary noble metal catalyst by OMG at 600–700°C. For iso-octane, intermediate hydrocarbons ethane and ethylene were observed. Methane was only observed in small amounts, but this appears not to be formed through methanation of carbon monoxide or carbon dioxide but either directly from hydrocarbons or by hydrogenolysis instead. During reforming of toluene benzene was detected, and the authors concluded that steam reforming of toluene starts by steam dealkylation, producing benzene:



Reforming of benzene then proceeds by break-up of the aromatic ring. Since no other hydrocarbons were detected, benzene is apparently converted in a single reaction step:



Wang and Gorte (2002) used platinum and palladium based catalysts for pre-reforming experiments with several hydrocarbons in the range of methane to toluene at 347–497°C. At these temperatures, no cracking products were observed. However, with larger molecules and differential conditions, cyclohexane is a major product, which indicates that C-C bonds remain largely intact on the catalyst surface. Differential measurements indicated that CO is a primary product, whereas cyclohexane and toluene resulted in benzene intermediates.

Modelling kerosene reforming, Kobori et al. determined kinetic parameters for the steam reforming of several hydrocarbons and mixtures of hydrocarbons over a ruthenium-based catalyst at 550–750°C. (Kobori, 2003) The product gas was found to be always at water-gas shift and methanation equilibrium and no significant amount of intermediates was detected, even at low

conversion. The kinetic parameters are shown in Table 3.1. Mesitylene showed the lowest reaction rate, suggesting a low reaction rate for aromatics in general. Addition of mesitylene to dodecane induces increased activation energy and a decreased reaction rate. Apparently, mesitylene is preferentially adsorbed on the catalyst surface and retards the activation of dodecane.

Table 3.1 *Kinetic parameters for steam reforming of kerosene and model components over a ruthenium catalyst at 550–750°C (Kobori, 2003)*

Fuel	E_a [kJ/mol]	Reaction orders	
		Hydrocarbon	H ₂ O
Kerosene	59	0.7	0.2
5% Mesitylene in dodecane	58	–	–
Dodecane	50	0.6	0.2
Mesitylene	36	0.7	0.3

In modelling the auto-thermal reforming of gasoline, Acharya, Lane and Krause (2006) performed a kinetic study of i-butane steam reforming over platinum supported on cerium-gadolinium oxide (CGO). Best fit of experimental data was found with a Langmuir-Hinshelwood expression:

$$r_{C_4H_{10}} = k_0 e^{-\frac{E_a}{RT}} \frac{K_1 K_2 P_{C_4H_{10}} P_{H_2O}}{1 + K_1 P_{C_4H_{10}} + K_2 P_{H_2O}^2} \quad (24)$$

$$k_0 = 32. \quad \text{mol/s g}_{\text{cat}} \text{ atm}^2 \quad K_1 = 2811. \quad \text{atm}^{-1}$$

$$E_a = 100. \quad \text{kJ/mol} \quad K_2 = 406. \quad \text{atm}^{-1}$$

Experiments showed a non-monotonic dependence of the reaction rate on the partial pressure of steam in the range of 0.3–0.95 atm, indicative of the blocking of active sites by adsorbed water molecules.

4. Pre-reforming Catalyst Degradation

Both nickel and precious metal pre-reforming catalysts degrade over time. The degradation of nickel based pre-reforming catalysts is related mainly to three phenomena: i) poisoning by sulphur, ii) fouling by deposition of carbonaceous deposits, and iii) sintering, depending on temperature. (Bartholomew, 2001; Christensen, Rostrup-Nielsen, 1996) Piwetz et al. (1996; Rostrup-Nielsen, Christensen & Dybkjaer, 1998) developed and operated a fuel processor for heavy logistic fuels. They report that the size of the pre-reforming catalyst bed is primarily determined by poisons in the feed stream, mainly sulphur, and by gum formation from diesel. Rostrup-Nielsen, Dybkjær and Christiansen (1993) report the adiabatic pre-reforming of heavy naphtha feedstock with a final boiling point of 220°C and an aromatics content of 30%. Progressive deactivation was observed mainly due to sulphur poisoning.

4.1 Poisoning

Poisoning is the strong chemisorption of species on active sites that renders the active sites inaccessible to other molecules. Whether or not the adsorption of a component is classified as poisoning of course depends on nature of the process. For example, water is a reactant in the pre-reforming reaction and its adsorption on the catalyst surface is of high importance to obtain sufficient activity and stability for many catalysts. On the other hand, water may also act as a poison if it adsorbs too strongly and blocks sites that are required for the adsorption of hydrocarbons. In this respect, hydrocarbons and water are not generally considered poisons for pre-reforming catalysts but under some conditions they might be. Especially unsaturated hydrocarbons, present in diesel, adsorb strongly on active sites and therefore can be considered poisons. (Bartholomew, 2001)

The activity of diesel pre-reforming catalysts is seriously affected by poisoning. Most notably, the feedstock in general contains significant quantities of sulphur, which can only be economically removed down to a level of several ppb. The remaining sulphur is known to slowly yet progressively poison the pre-reformer catalyst. Other poisons such as alkali metals, silica, arsenic, and phosphorus may also be present in the hydrocarbon feedstock. (Christensen, 1996) Silica physically blocks the entrance to the catalyst pores. Alkali metals that are deposited on the catalyst cause a marked decrease in the turnover frequency (cf. Section 2.1.3). The poisoning effect of alkali metals is stronger on less acidic supports. (Christensen, Rostrup-Nielsen, 1996)

Especially nickel-based pre-reforming catalysts are strongly poisoned by sulphur. Sulphur compounds are reversibly yet strongly chemisorbed at the metal surface and are a severe poison for steam reforming catalysts:



The equilibrium depends on temperature and gas phase composition, while both vary throughout the reactor and within the catalyst pellet. The isosteric heat of adsorption is approximately 155 kJ/mol while the heat of formation of bulk sulphide Ni_3S_2 is about 75 kJ/mol. (Rostrup-Nielsen, 1984) The sulphide is bound to the nickel surface relatively strongly and consequently a surface sulphide can be stable at conditions where bulk sulphide does not exist. For example, at 450°C, Ni is almost completely covered by sulphur ($\theta > 0.9$) at $\text{P}(\text{H}_2\text{S})/\text{P}(\text{H}_2)$ -ratios of only $10^{-7} - 10^{-6}$, i.e. in the ppmv range of H_2S . (Bartholomew, 2001)

Due to significant axial and intraparticle gradients of both temperature and hydrogen partial pressure in industrial reformers, the distribution of sulphur in the catalyst bed is complex. Christensen and Rostrup-Nielsen (1996) cite earlier work performed at Haldor Topsøe, determining the equilibrium sulphur coverage of H_2S on $\text{Ni}/\text{MgAl}_2\text{O}_4$ as:

$$\vartheta = 1.45 - 9.53 \cdot 10^{-5} T + 4.17 \cdot 10^{-5} T \ln \left(\frac{p_{H_2S}}{p_{H_2}} \right) \quad (26)$$

On top of the strong affinity of sulphur for nickel, the poisoning by H₂S is highly selective: step sites on the nickel crystals that are the most active sites are preferentially occupied by sulphur. (Shekawat, 2006) As a consequence, Ni catalysts may suffer a loss in activity of three to four orders of magnitude in presence of only 15-100 ppb of H₂S. (Bartholomew, 2001) The effect on the observed reaction rate may, according to Christensen and Rostrup Nielsen (1996), be predicted by:

$$r_{\text{effective, poisoned}} = (1 - \vartheta_{\text{av}})^\alpha r_{\text{effective, unpoisoned}} \quad (\text{or: } r_{\text{intrinsic, poisoned}} = (1 - \vartheta)^3 r_{\text{intrinsic, unpoisoned}}) \quad (27)$$

The poisoning of pre-reforming catalysts by sulphur will be pore diffusion limited and therefore proceed in an egg-shell fashion. The outer surface of the catalyst particles will be in equilibrium with the bulk gas phase while a sharp decrease in coverage is formed towards the centre of the particles. (Christensen, 1996; Christensen, Rostrup-Nielsen, 1996)

The highly selective poisoning by sulphur has even found application in so-called "sulphur-passivated steam reforming". The nickel step sites that are preferentially poisoned by sulphur are also the most active for carbon forming reactions. (Bengaard, 2002; Shekawat, 2006) It is possible to reduce carbon formation through selective poisoning of important coke forming sites by sulphur. However, the sulphur drastically lowers the catalytic activity for the steam reforming reaction as well and high reaction temperatures are required to compensate for the lowered activity. (Rostrup-Nielsen, 1984) It is not a viable option for adiabatic pre-reforming processes. In contrast, sulphur is even known to enhance catalyst deactivation by promoting coke formation. Sulphur possibly enhances the transformation of chemisorbed carbon into carbon film, either by catalysing the process itself or by preventing dissociative adsorption of H₂ and thereby poisoning the hydrogenation of chemisorbed carbon. Sulphur is also linked to the change in selectivity in CO methanation to hydrogen-poor products, which result in coke and carbon on the surface. (Bartholomew, 1982)

The addition of molybdenum or boron has been reported to improve the resistance of nickel reforming catalysts to sulphur poisoning. (Bartholomew, 2001)

Precious metals are much less affected by sulphur poisoning than nickel catalysts. However, little data is available in open literature. Lu et al. (2008) have shown that their Pt/Ce_{1.9}Gd_{0.2}O_{1.9} catalyst is able to tolerate up to 500 ppmw of thiophene in iso-octane reforming at 750°C. At lower temperatures the effect of sulphur is more severe. Strohm, Zheng, and Song (2006) extensively investigated sulphur tolerance in pre-reforming of jet fuel over rhodium and rhodium-nickel catalysts at low temperature (< 520°C). Monometallic Rh/CeO₂-Al₂O₃ catalysts suffered from sulphur poisoning during reforming of feedstock with > 10 ppmw of sulphur. Especially the methanation activity rapidly deteriorates in presence of sulphur. Addition of nickel to the rhodium catalyst leads to an increased sulphur tolerance: nickel acts as protective and even sacrificial metal. Bimetallic Rh-Ni/CeO₂-Al₂O₃ catalyst allows for successful pre-reforming of JP-8 jet fuel with 22 ppm of sulphur for up to 72 hours.

4.2 Fouling by carbon and coke

Under operating conditions, deposits may form on the catalyst surface, which is called fouling. Fouling easily leads to degradation of the catalyst because active sites or even catalyst pores can be blocked. If fouling continues it may even break down catalyst particles and clog parts of the reactor. In reforming and pre-reforming processes, fouling is mainly caused by formation of carbonaceous deposits, which is the subject of this section. These deposits either are carbon or coke, depending on their origin. Coke is formed from decomposition and/or polymerisation of

hydrocarbons while carbon is formed by the CO disproportionation reaction. (Bartholomew, 2001)

4.2.1 Types of deposit

McCarty et al have devised a classification of the types of coke that are formed on nickel reforming catalysts that has been widely adopted in ensuing publications on the subject. (McCarty, 1982) The different types of carbon that form on reforming catalysts can be determined efficiently through temperature-programmed reduction (TPR) of spent catalyst samples in hydrogen. The catalyst samples are heated with a constant rate from room temperature to about 1000°C in hydrogen. During the process, carbonaceous species are reduced to methane at a temperature that is indicative of the type of species involved. Either the hydrogen consumption or the methane production can be plotted against temperature, showing peaks that are characteristic of the types of carbon on the sample. The experiments were based on two commercial nickel catalysts from United Catalysts, one with 17% w/w and another with 25% w/w, both on alumina support. Carbon was formed by exposure to C₂H₄, and by exposure to CO. The methane production peaks identified by TPR are reproduced in Table 4.1.

Table 4.1 *Methane production peaks during TPR of nickel catalysts with 1 atm H₂ after exposure to C₂H₄ and CO (McCarty, 1982, Table IV)*

Carbon state	Identification	Peak temperature [K] at maximum rate	
		C ₂ H ₄ exposure	CO exposure
α'	Reactive carbon	410 ± 15	380 ± 15
α	Chemisorbed carbon	480 ± 25	460 ± 20
β	Carbon film	660 ± 30	660 ± 20
γ	Ni ₃ C	~ 550	~ 480
δ'	Carbon filaments	875 ± 20	850 ± 40
δ	Encapsulating carbon	960 ± 15	–
ε	Platelet carbon	1120 ± 20	–

Christensen and Rostrup-Nielsen (1996) have applied the same TPR procedure to spent pre-reforming catalysts (Ni/MgO), both from laboratory and industrial reactors. They were able to assign the peaks to six different species, closely matching the results by McCarty et al. The carbon morphologies are shown in Table 4.2.

Table 4.2 *Carbon morphologies on adiabatic pre-reforming catalysts as determined through H₂-TPR (heating rate 6°C/min) (Christensen, Rostrup-Nielsen, 1996, Table II)*

	Peak temperature (°C)	Carbon type	Carbon morphology
1	190 – 205	α'	chemisorbed carbon
2	260 – 300	α	chemisorbed carbon
3	420 – 530	β	gum / β carbon film *
4	570 – 600	δ	filamentous carbon
5	630 – 720	ε	platelet / pyrolytic carbon
6	950 – 1000	G	graphitised carbon

* The gum (β carbon) peak is generally very broad as the polymerisation deposits will contain varying amounts of hydrogen.

Many types of carbon form on pre-reforming catalysts, depending on operating conditions and feedstock. Not all types of carbon deactivate the catalyst, however. C_α, for example, is believed to be a critical intermediate in many reactions. (Trimm, 1997b) McCarty et al. (1982) present an overview based on TPR experiments and literature review that is reproduced in Table 4.3. As

pre-reformers operate at characteristically low temperature the main carbon forms to be expected are gum (β carbon) on the one hand, and whiskers (δ) on the others. Besides temperature, it is mainly the steam to carbon ratio and the feedstock composition in terms of aromatics and olefins that determine carbon deposition on a given catalyst. The window of operation for a pre-reformer is to a large extent determined by the gap between these two forms of carbon deposition.

Table 4.3 *Deactivation characteristics of carbon deposits on nickel hydrocarbon reforming and synthesis catalysts (Rostrup-Nielsen, Tothrup, 1979; McCarty, 1982 and references therein)*

Carbon state	Carbon morphology	Mechanism of formation	Effect on catalyst and reactor	Parameters favouring deposition
β	Film	Slow polymerisation of CH_x radicals on Ni surface	<ul style="list-style-type: none"> • Progressive, reversible deactivation • Little carbon buildup 	<ul style="list-style-type: none"> • Low T (<770K) • Low $\text{H}_2\text{O}/\text{C}$ • Low H_2/C • Aromatics and olefins in feed
δ'	Filaments / whiskers	Diffusion of C through Ni crystallite and precipitation at the back, creating filaments carrying the crystallite	<ul style="list-style-type: none"> • No deactivation • Catalyst breakdown • Rapid increase in pressure drop • Massive deposit 	<ul style="list-style-type: none"> • High T (>720K) • Low $\text{H}_2\text{O}/\text{C}$ • Low H_2O adsorption • Aromatics and olefins in feed • Low activity
δ	Encapsulating shell	Similar to filament, but layers precipitate and grow on all crystal planes	<ul style="list-style-type: none"> • Deactivation • Slow carbon buildup 	<ul style="list-style-type: none"> • High T (>800K) • Low $\text{H}_2\text{O}/\text{C}$
ϵ	Platelet	Precipitation of crystalline graphite from dissolved carbon	<ul style="list-style-type: none"> • Deactivation • Small carbon buildup • Difficult to remove 	<ul style="list-style-type: none"> • High T (>900K) • Low pressure • Ageing deposit
G	Pyrolytic	Thermal cracking of hydrocarbon and deposition of carbon precursors on catalyst surface	<ul style="list-style-type: none"> • Encapsulation of catalyst particles • Deactivation by pore blocking • Increased pressure drop 	<ul style="list-style-type: none"> • High T (>870K) • Low $\text{H}_2\text{O}/\text{C}$ • High void fraction • High pressure • Low space velocity • Acidic support
G	Soot	Homogeneous nucleation and growth of carbon particles	<ul style="list-style-type: none"> • Increased pressure drop • Large carbon deposit 	<ul style="list-style-type: none"> • High temperature • High pressure • Low reforming activity • Low space velocity

4.2.2 Gum

The enhanced formation of gum has long been recognised to be the main problem in processing heavier feedstock at relatively low temperatures. (Jockel, 1969; Davies, Templeman & Wragg, 1975) Gum or β -carbon (cf 4.2.1) consists of condensed polymers that are generally formed at temperatures below 375°C. (Bartholomew, 2001) The composition of the feedstock as well as process parameters however strongly influence gum formation.

Higher hydrocarbons are adsorbed on the metal surface and subsequently polymerise through a sequence of surface reactions. The chemical structure of the polymers changes from $(-\text{CH}_2-)_n$ into aromatics as the polymers are dehydrogenated. (Rostrup-Nielsen, 1984) Jackson et al. (Jackson, Thomson & Webb, 1981) found linear, hydrogenated polymers with 25-30 carbons chain length. In presence of steam aldehyde groups had been formed as part of the chains. Polycyclic aromatics such as naphthalene, anthracene, and pyrene have been found in other gum deposits. (Rostrup-Nielsen, Tottrup, 1979) The polymer products can increase in molecule size through incessant reactions and may eventually encapsulate the active metal. Once gum formation is observed, deactivation of the catalyst will generally proceed very fast. In fact, deactivation by gum formation can proceed several times faster than ordinary poisoning. (Christensen, 1996; Christensen, Rostrup-Nielsen, 1996)

The high molecular weight molecules of gum are thermodynamically unstable and their formation is solely governed by kinetics. Kinetics of gum formation depends on the relative rates of two reactions: the rate of adsorption of higher hydrocarbons on the catalyst surface on one hand and the rate of carbon-carbon bond cleavage on the other. (Christensen, 1996) The risk of gum formation is therefore directly related to these two phenomena: it increases with decreasing temperature, low steam to carbon ratio, low hydrogen content of the feed and higher hydrocarbon boiling point. (Davies, Templeman & Wragg, 1975; Christensen, 1996; Sperle, 2005) The addition of hydrogen to the pre-reforming process will shift the methanation equilibrium and therefore makes to process more exothermal. Recirculation, however, has been applied to effectively reduced gum formation in processing heavy feedstock as well, without raising the adiabatic temperature rise. (Davies, Templeman & Wragg, 1975; Rostrup-Nielsen, Tottrup, 1979)

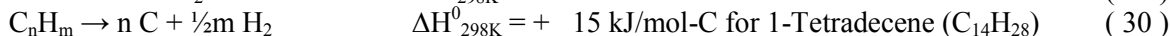
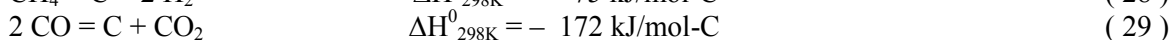
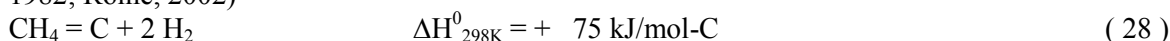
Gum formation is generally only found below 500°C and it increases with decreasing temperature as the rate of carbon-carbon cleavage decreases more strongly with temperature than the rate of adsorption. Gum formation is enhanced by low steam to hydrocarbon ratios and low hydrogen content because low steam and hydrogen concentrations decrease the gasification rate. For adiabatic pre-reforming of diesel, the steam to carbon ratio must be about 2.5 with a hydrogen-to-carbon ratio of about 0.3 in order to achieve only slow gum formation. (Christensen, 1996) Hydrocarbons with a higher boiling point as well as aromatics will adsorb more strongly onto the catalyst surface and therefore increase the risk of gum formation. Experimental observations indicate the presence of sulphur is also linked to increased gum formation. (Bartholomew, 1982; Christensen, 1996; Piwetz, Larsen & Christensen, 1996; Christensen, 1996; Hansen, 2005)

As the determining factors are rather complex, experiments are required to determine the temperature boundary for gum formation for a specific combination of catalyst, feedstock, and process parameters. Haldor Topsøe tested diesel and jet fuel in an adiabatic pre-reformer over a high surface area nickel catalyst supported on magnesia. The feeds were desulphurised down to 0.5-1 ppm (w/w) of sulphur. The process was demonstrated for 500-1,000 hours, at acceptable resistance numbers (S-tolerance, cf Section 4.4.1). For jet fuel, no gum was formed and the catalyst only deactivated by sulphur poisoning. For diesel, slow gum formation was observed near the lower temperature limit of the window of operation. The top part of the catalyst bed was tested in subsequent intrinsic activity measurements and showed a gum deactivation factor of 5. (Bartholomew, 1982)

4.2.3 Whiskers

The formation of carbon whiskers (δ' , cf 4.2.1) occurs at intermediate temperatures of 375–650°C. Carbon whiskers are formed by precipitation of dissolved carbon from the metal particles. This process typically leads to filaments of carbon with a nickel particle on top. As this does not necessarily block the accessibility of the nickel surface, formation of filamentous carbon does not necessarily cause catalyst deactivation. It may even increase the activity because of a redispersion of the nickel on the carbon support. (Rostrup-Nielsen, Tottrup, 1979) However, excessive filaments may bring about plugging of pores and even breakdown of the catalyst particles. In addition, filamentous carbon ($C_{\delta'}$) may grow into encapsulating carbon (C_{δ}), causing catalyst degradation.

The composition of the whisker is very close to graphite: it contains little or no hydrogen. (Bartholomew, 1982; Rostrup-Nielsen, 1984; Christensen, 1996) The carbon is formed during the process by dissociation of methane, carbon monoxide, and hydrocarbons. (Bartholomew, 1982; Roine, 2002)



(C as graphite, see below) In general, rate of the latter reaction decreases in the order: acetylenes > olefins > paraffins and may prevail in the pre-reforming of feedstock containing significant amounts of unsaturates, such as diesel. While the rates for benzene and toluene are orders of magnitude larger than the rate for CO, the same mechanism is probably occurring. Filaments formed by hydrocarbon decomposition are structurally very similar to those formed by CO disproportionation. (Rostrup-Nielsen, Christensen & Dybkjaer, 1998; Bartholomew, 2001)

Supported cobalt, iron, and nickel are all known to be active for the formation of filamentous carbon both from carbon monoxide and from hydrocarbons. Platinum, ruthenium, and rhodium catalysts, on the other hand, form little or no filaments. (Rostrup-Nielsen, 1984)

The assessment of carbon whisker formation must be based upon two aspects: thermodynamics as well as kinetics. Thermodynamically, carbon will be formed if the equilibrium of reactions (28) and (29) lies towards the right hand side when the gas phase is at equilibrium. This calculation is sometimes referred to as the principle of equilibrated gas. As a consequence, the tendency for carbon deposition is governed by the ratios O/C, H/C, inert/C, and the temperature and total pressure. (Bartholomew, 1982)

Thermodynamics relates the tendency for carbon formation to the chemical potential of the species involved in the reactions. The calculation of the potential for carbon deposition is not very straightforward, though. Major deviations from predicted equilibrium may occur if the gas contains other species such as higher hydrocarbons. (Ross, 1975; Bartholomew, 1982; Christensen, 1996) Additional complexity arises from the fact that derivation of the chemical potential of the carbon phase is not straightforward. The exact shape of the deposits plays an important role and the highly non-ideal structure of the whiskers must be known and taken into account properly. (Rostrup-Nielsen, 1984) In fact, carbon deposits are generally less favourable than plain graphite because of the whisker shape. Small nickel particles create small whiskers with a relatively high free energy. (Bartholomew, 1982) On the other hand the surface roughness plays an important role. Filamentous carbon is favoured on rough surfaces in general and less favoured on single crystals without grain boundaries. The formation of carbon could therefore be enhanced on small particles having a higher frequency of rough planes. (Rostrup-Nielsen, 1984)

Thermodynamics provides a possibility to evaluate the risk of carbon formation, but it cannot guarantee carbon-free operation. Coke may be formed due to poor activity or selectivity of the catalyst, even if the equilibrium composition predicts no carbon. Kinetics therefore plays a crucial role in the prediction of whisker formation as well. Thermogravimetric studies of carbon deposition (cf Figure 4.1) have helped to relate the formation of whiskers to an induction period

(of little carbon formation), followed by a period with a constant coking rate: (Bartholomew, 1982)

$$r_c = k_c(t - t_0) \quad (31)$$

Carbon formation from hydrocarbons and from CO follows the same characteristic induction period followed by 0th order increase. (Snoeck, Froment & Fowles, 1997) The generally accepted model for the growth of filaments is based upon diffusion of carbon atoms through the nickel particles. Driving force is the difference in chemical potential between the gas phase and the carbon filament, causing a difference in solubility of C in Ni and therefore a concentration gradient. (Rostrup-Nielsen, 1984) Nucleation of carbon at the back of the nickel eventually leads to a whisker of carbon with a nickel particle on top. At low temperatures the diffusion is rate determining. (Bartholomew, 1982) The process continues until the metal particle is encapsulated. Induction period is the required time for dissolution, diffusion, precipitation, and separation of the crystallite from the support. (adapted from Rostrup-Nielsen, 1984)

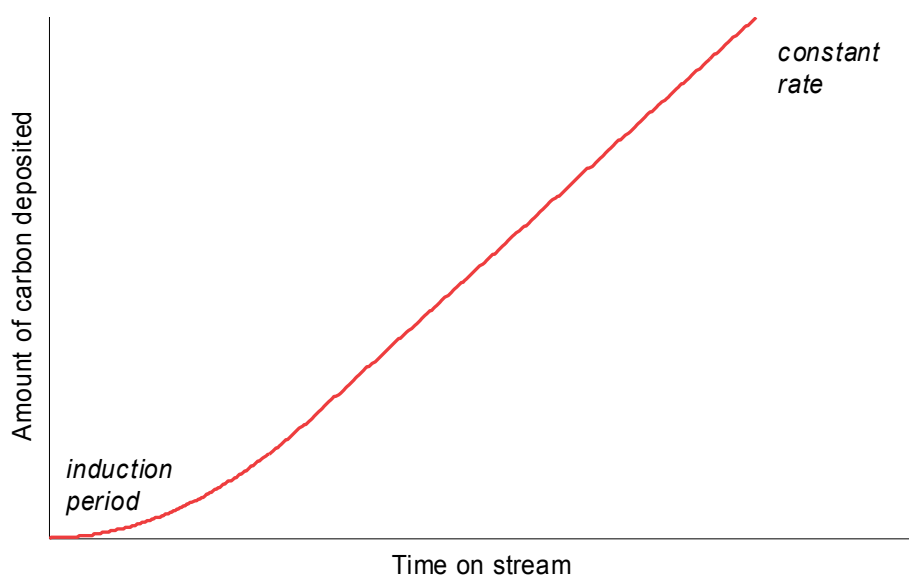


Figure 4.1 *Carbon deposition as a function of time from hydrocarbons on nickel (Rostrup-Nielsen, Tottrup, 1979)*

4.2.4 Pyrolytic coke

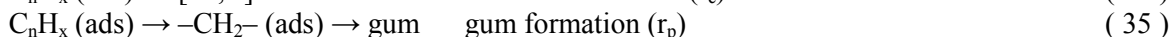
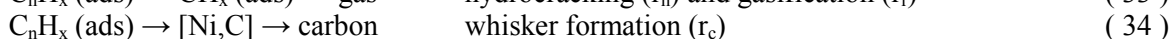
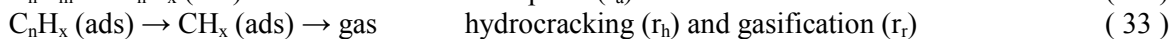
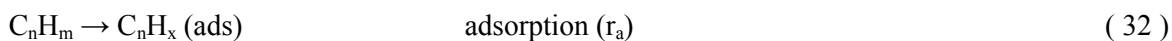
Encapsulation of particles by the products of thermally cracked hydrocarbons, pyrolytic coke, is encountered above 600°C. Pyrolytic coke is formed by the deposition of tar-like components and may contain significant amounts of hydrogen, in contrast with whisker carbon. For pyrolytic carbon, Rostrup-Nielsen and Tottrup (Bartholomew, 2001) mention a C/H ratio in the order of 20.

The formation of pyrolytic coke is enhanced by adsorbed sulphur at the catalyst surface. The sulphur creates acid sites that catalyse cracking reactions of typical coke precursors such as olefins and aromatics. These acid sites form carbocations that readily initiate dehydrogenation and cyclisation reactions. (Bartholomew, 2001) The chemistry of coke formation is reflected in the structure dependence: polynuclear aromatics > aromatics > olefins > branched alkanes > normal alkanes. (Rostrup-Nielsen, Tottrup, 1979; Christensen, Rostrup-Nielsen, 1996) However, since pre-reforming is performed at lower temperatures the formation of pyrolytic coke is not considered a problem for this process.

4.2.5 Mechanisms and Kinetics

Whisker carbon is formed for a given feedstock, catalyst and process conditions above a certain temperature: $T \geq T_c$. Gum, on the other hand, is formed by the polymerisation of hydrocarbons (especially unsaturates and aromatics) on the catalyst surface and it takes place at low temperatures: $T \leq T_p$.

Gum formation likely proceeds through polymerisation and gradual dehydrogenation of adsorbed hydrocarbons. The adsorbed species are converted into less reactive residues on the catalyst surface, e.g. paraffins may be converted into aromatics. A simplified kinetic sequence can be formulated (Bartholomew, 1982) according to:



The risk of carbon formation depends on the type of hydrocarbon, on the catalyst and on process conditions. Ethylene and benzene chemisorb more easily and hydrocrack less easily than paraffins. In conclusion, the content of unsaturated hydrocarbons and aromatics is a crucial parameter for carbon-free operation in steam reforming of heavy hydrocarbons. Both H_2 and H_2O are very effective in the reduction or even elimination of the formation of carbon or the deposition of coke. Adsorbed H_2 or H_2O react with and thus remove adsorbed carbon and coke precursors. If sufficient H_2 or H_2O is present, the surface residence time of active carbon species and coke precursors will be too short to allow measurable transformation of these species to more inactive forms. Best reforming catalysts are therefore active for the adsorption of both hydrocarbons and water and achieve an even balance between the rate of formation of adsorbed carbon and coke precursors and of their gasification by adsorbed water. (Rostrup-Nielsen, 1984) Normal alumina-based catalysts for steam reforming of natural gas have low values for the adsorption of water and cannot operate with liquid hydrocarbon fuels. One solution is to promote with alkali, enhancing water adsorption at the expense of a drastic decrease in the activity of the catalyst. Another solution has been the use of active magnesia for enhanced steam adsorption. Crystal size may play a role as well, possibly related to the spill-over of water from the support onto the nickel. (Rostrup-Nielsen, 1984; Christensen, 1996)

In an empirical approach, whisker carbon formation is expected, for a given feedstock and temperature, below a critical steam to hydrocarbon ratio:

$$\left(\frac{P_{H_2O}}{P_{C_nH_m}} \right)_{crit.} = -\frac{a}{T} + b \quad (36)$$

Coke formation is expected below the critical steam-to-hydrocarbon ratio. Constants a and b strongly depend on both catalyst and feedstock composition (Rostrup-Nielsen, Tottrup, 1979; Christensen, Rostrup-Nielsen, 1996) and no values have been reported in open literature. However, the ratio was found to increase rapidly with temperature and to be influenced by the type of hydrocarbon as well as by the catalyst. (Rostrup-Nielsen, Tottrup, 1979) As a consequence, there is a whisker formation temperature T_c , above which whiskers are formed.

Normally the pre-reforming process is performed at low temperatures to ensure $T < T_c$ and formation of carbon whiskers is effectively prevented. This means that, in practical applications, $r_c = 0$ and consequently $r_p = r_a - r_h$: the rate of gum formation equals the difference between the rate of adsorption and the rate of hydrocracking. The relative rates of adsorption and hydrocracking both depend on temperature, yet not equally. The activation energy for adsorption of hydrocarbons on nickel is 40 kJ/mol, while the activation energy for hydrocracking is 160–260 kJ/mol, depending on the hydrocarbon involved. (Rostrup-Nielsen, Christensen & Dybkjaer, 1998) Consequently, there will be a temperature T_p , corresponding to $r_a = r_h$. Below

$T_p, r_a > r_h$ and gum will be formed. To ensure trouble free operation, the temperature must be in the kinetically determined window of $T_p < T < T_c$, as shown in Figure 4.2. Aromatics, present in heavy fuels such as diesel, tend to narrow the gap by decreasing T_c and increasing T_p . Moreover, it also causes a decrease in activity while a higher operating temperature means that the process will become more critical to coking. (Sehested, 2003)

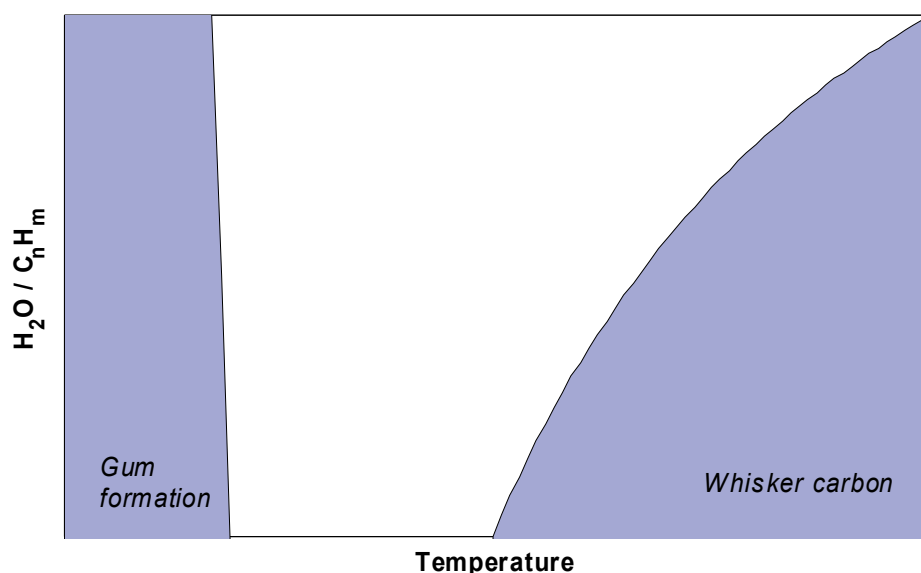


Figure 4.2 *Temperature window for carbon-free pre-reforming (Christensen, Rostrup-Nielsen, 1996)*

4.3 Sintering

Thermal degradation of the catalyst can occur because small metal particles on an oxidic support have a tendency to sinter, i.e., form larger metal particles and decrease the available metal surface area. The high energy of exposed metallic surfaces drives the sintering process. (Chorkendorff, Niemantsverdriet, 2003) According to Tamman's rule, volume diffusion of nickel particles may occur above their Tamman temperature of 591°C, i.e. half the melting temperature (in Kelvin) of metallic nickel. (Trimm, 1997a) Relevant precious metals have higher values of the Tamman temperature. The presence of steam may further enhance sintering and it must therefore be taken into account for pre-reforming processes as well. For example, Sehested et al. (2001) experimentally found significant sintering of nickel particles on $MgAl_2O_4$ at a temperature as low as 500°C, at 30 bar total pressure and steam:hydrogen 10:1. Generally, two mechanisms are proposed for the sintering of metal particles: atom migration (Ostwald ripening) and particle migration (coalescence). (Wynblatt, Gjostein, 1975) Ostwald ripening refers to a process where metal atoms are emitted from one metal particle and captured by another metal particle. In the particle migration process, the particles themselves move over the support and collide to form larger particles. The coalescence process is rapid and hence the migration becomes rate determining. (Sehested, 2003) When particles are small and particle migration is rate controlling, the important parameters determining the growth rate are surface initial average particle density and diffusion rate. (Wynblatt, Gjostein, 1975)

Loss of active sites may also occur through the sintering of the catalyst support, especially since carriers with high surface area are used. Thermal stability of the support is therefore important. (Christensen, Rostrup-Nielsen, 1996)

4.4 Predictive Modelling of Catalyst Degradation

Deactivation of pre-reforming catalysts cannot normally be prevented and catalyst lifetime in industrial processes is limited to 2–3 years. In order to assess catalyst deactivation, both empirical and modelling techniques are available for prediction of deactivation. (Rostrup-Nielsen, 1984)

4.4.1 Empirical modelling

Empirical modelling can be done based on the temperature profile that is observed in the pre-reforming during operation. As explained in Section 1.2, the pre-reforming process consists of consecutive endothermic and exothermic reactions, leading to a characteristic temperature profile. Typical temperature profiles, or reaction fronts, are reproduced in Figure 4.3. During progressive deactivation, for example by sulphur poisoning or gum formation, the reaction front will gradually lengthen. The length of the profile can therefore be used to assess and even extrapolate catalyst degradation.

Since the length of the entire temperature profile is difficult to determine exactly, ΔT_{90} is defined as 90% of the total temperature rise from inlet to outlet and z_{90} is defined as the distance from the reactor inlet where ΔT_{90} is reached (cf. Figure 4.3). Following the procedure outlined by Christensen and Rostrup-Nielsen (Moseley, 1972), the length of the reaction front can be plotted against time on stream as shown in Figure 4.4. This deactivation plot will generally approach a straight line after an initial period of more rapid deactivation. Once the deactivation plot has become straight it can be extrapolated in order to estimate the expected catalyst lifetime. A resistance number R can be defined as the inverse slope of the deactivation plot (e.g., as the kilograms of feedstock required to deactivate one gram of catalyst), which means that a large resistance number corresponds to a slowly deactivating catalyst. After an initial period of relatively fast deactivation, industrial conditions result in a nearly constant value of the resistance number around 5–20 kg/g. (Christensen, Rostrup-Nielsen, 1996)

Using this approach, Moseley et al. (Christensen, Rostrup-Nielsen, 1996) found large resistance numbers for high S/C, high p_{H_2} , high H/C in the feed; low T causes a decrease in R . Aromatics in the feedstock tend to lower R , because they have a high rate of adsorption (r_A) and low rate of hydrocracking (r_h).

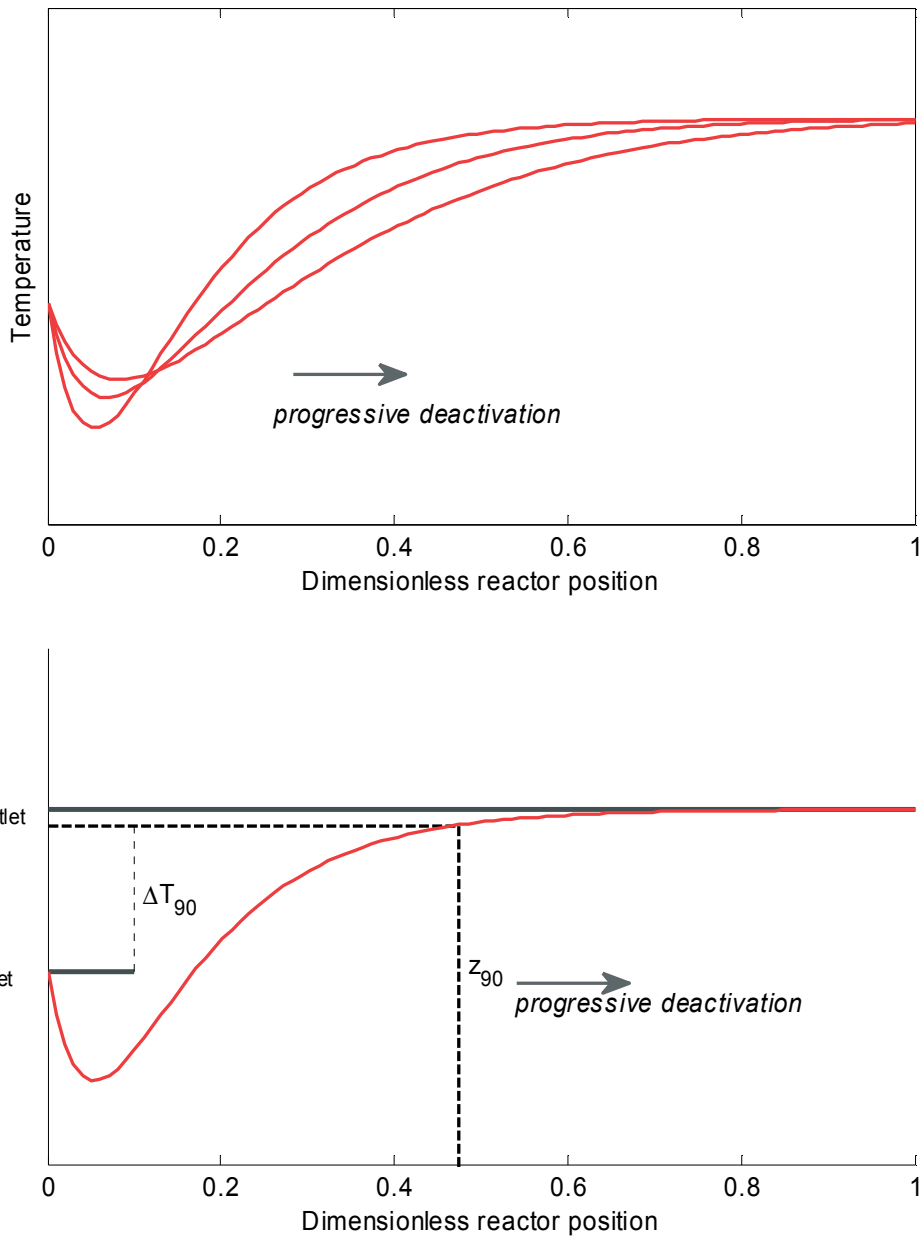


Figure 4.3 Pre-reformer temperature profiles and characteristics ΔT_{90} and z_{90}

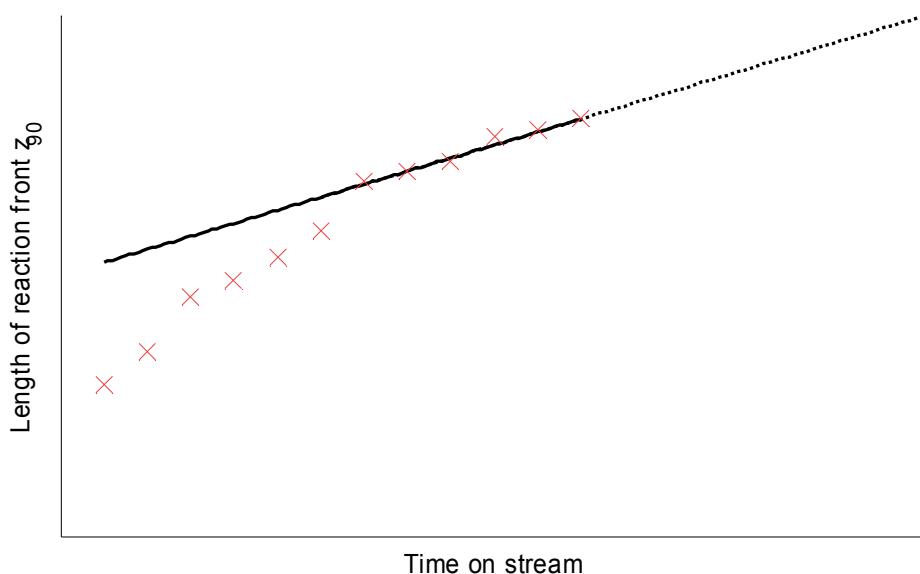


Figure 4.4 *Length of the reaction front z_0 plotted versus time on stream, eventually approaching a straight line that allows extrapolation*

Bench-scale testing is a valuable tool to investigate the impact of deactivation on catalyst performance. Full-size pellets, industrial mass velocity, and pressure are used. Application of pseudo-adiabatic reactors ensures reliable adiabatic testing. Using adiabatic experiments and the graphical deactivation plot technique, it was shown (Christensen, Rostrup-Nielsen, 1996; Christensen, 1996) that fast deactivation occurred for 200 hours whereupon it stabilises at a lower activity level. Initial sulphur poisoning affects the outer surface of the catalyst pellets, having the highest impact on apparent activity. The overall resistance number was about 40 kg-feedstock/g-catalyst – which is in the normal range. Temperatures showed a continually decreasing endothermic dip, indication of low rate gum formation, confirmed by post-test analyses. In spite of the gum formation, an acceptable resistance number was obtained.

In addition, ex situ analysis of pre-reforming catalysts can lead to crucial information on degradation, such as the degree of sulphur poisoning (cf. Section 4.1) or the types of carbon that have been deposited (cf. Section 4.2). Haldor Topsøe has determined the intrinsic activity for ethane steam reforming in order to establish catalyst deactivation. (Jockel, 1969)

4.4.2 Numerical modelling

Alternative to the empirical modelling approach of the previous section, numerical modelling may also be used for the prediction of catalyst degradation behaviour. Christensen and Rostrup-Nielsen of Haldor Topsøe mention the predictive numerical modelling of catalyst deactivation. (Bartholomew, 1982) Their computer simulations require thorough knowledge of process fundamentals as they have been based on pore diffusion and poisoning models combined with kinetic models. Satisfactory results are claimed in describing the adiabatic pre-reforming process both on a bench scale and on an industrial scale. Nevertheless, numerical modelling of adiabatic pre-reforming can only be successful in case the relevant process parameters are well known, i.e. based on a substantial amount of experimental work.

4.5 Catalyst Regeneration

Regeneration of degraded pre-reforming catalysts may be possible, but carbon deposition and sulphur poisoning are in general more easily prevented than cured.

Polymerisation products can be removed by either oxidative or reductive regeneration. (Rostrup-Nielsen, 1975) Gasification by steam is reasonably fast, but works for relatively fresh carbon only. Aged carbon is only removed upon the addition of some oxygen as well. Gasification of amorphous carbon by hydrogen is much slower. Regeneration by means of oxygen only is not feasible option. It easily causes loss of the active metal because of combustion of the carbon that is present between the nickel particle and the support.

Besides removal of carbon or coke, sulphur poisoning must be cured as well. Unfortunately the chemisorption of H_2S on nickel appears unaffected by the partial pressure of steam and complete regeneration by means of reverse chemisorption with hydrogen may be slow. However, sulphur may be easily removed by steaming at temperatures above $600^\circ C$, involving complete oxidation of the catalyst, and in absence alkali. (In presence of alkali, steaming results in formation of sulphates instead.) It is then possible to remove the sulphur in the oxidised state by a reduction process because nickel oxide is reduced at a rate lower than the rate of formation of hydrogen sulphide.

5. Conclusion

While it is far from being a conventional and well understood process, there is sufficient evidence from open literature to suggest that adiabatic diesel pre-reforming is feasible. From the adiabatic gasification of naphtha in the catalytic rich gas process in the 1950s and 1960s, the process has been developed over the last fifty years to cope with heavier feedstock, including diesel. Adiabatic pre-reforming is operated around 450–500°C. The sequence of endothermic steam reforming and exothermic water-gas shift and methanation reactions causes a typical temperature dip in adiabatic operation. During the process the temperature profile moves downstream because of catalyst degradation.

Pre-reforming of diesel can be done using two main types of catalysts: nickel-based catalysts and precious metal-based catalysts. Nickel is presently applied industrially in many pre-reforming processes, is significantly less expensive than precious metal, and its functioning is relatively well understood. Precious metals, on the other hand, may offer benefits in terms of a higher activity, better sulphur tolerance, and greater coking resistance. However, relatively little information can be found in the open literature on precious metal pre-reforming catalysts. A lack of sufficient experimental work presently precludes selection of a proper catalyst type for diesel pre-reforming for fuel processing applications.

5.1 Adiabatic diesel pre-reforming over nickel catalysts

By far the largest body of literature on heavy feedstock pre-reforming deals with nickel catalysts. Nickel is relatively inexpensive while still very active for reforming reactions and nickel catalysts are in industrial operation in numerous pre-reformers and steam reformers worldwide. Kinetics, catalyst activity, and deactivation all depend strongly on feedstock, process conditions and nature of the catalyst. In general, the process is operated at space velocities of 1,500 – 3,000 hr⁻¹.

At temperatures below 600°C, the mechanism appears to proceed through irreversible adsorption of higher hydrocarbons on metallic nickel sites. The carbon atoms subsequently react to CO, CO₂, and CH₄ – or remain on the catalyst as carbon/coke. A possible exception to this scheme may be benzene, which has been observed as an intermediate by some authors. Hydrogenation of cracking products or carbonaceous deposits may yield ethane, propane, etc., but the first requires elevated temperatures while literature evidence of the latter is limited. Kinetically, good fits of experimental data in limited range have been obtained using fairly simple power law rate equations including the partial pressures of hydrocarbon, steam, and possibly hydrogen. Following a mechanistic approach, scientists from Haldor Topsøe have successfully applied a rate equation including Langmuir adsorption, which possibly benefits from a wider range of validity.

Main issues with pre-reforming of heavy feedstock over nickel catalysts are related to catalyst deactivation by sulphur poisoning and coke deposition. Even desulphurised diesel may contain a few ppb up to 1 ppm of sulphur and sulphur strongly and selectively poisons active nickel sites. Sulphur poisoning causes progressive deactivation in the catalyst bed. The deposition of coke is strongly related to the feedstock used. Large and/or unsaturated hydrocarbons adsorb strongly on the catalyst surface and may easily form gum deposits. Gum deposits are formed at relatively low temperatures and may cause very fast catalyst deactivation by encapsulation of active sites. At high temperatures and low steam ratios carbon whiskers may be formed as well. Whiskers do not directly affect the catalyst activity, yet may eventually break down catalyst particles and cause plugging of the reactor. The temperature window between gum and whisker formation determines the operating temperature for the pre-reforming process. Based on a number of publications, it appears possible to operate an adiabatic diesel pre-reformer in such conditions that

the deactivation rate by sulphur poisoning and by coke deposition is acceptably low. After an initial period of more rapid deactivation, the deactivation appears to stabilise at a 'resistance number' of 5–20 kg/g (kilogram of feedstock per gram of catalyst deactivated).

5.2 Adiabatic diesel pre-reforming over precious metal catalysts

Precious metal catalysts may be a valid alternative to common nickel based catalysts. Among the potential benefits encountered in literature are a higher activity, better sulphur tolerance, and a greater coking resistance, while the main drawback is related to the price of precious metals. As with nickel, kinetics, catalyst activity, and deactivation all depend strongly on feedstock, process conditions and nature of the catalyst. Precious metal catalysts may have turnover frequencies up to an order of magnitude larger than nickel and precious metal catalysts have been applied at space velocities in the order of 10,000 hr⁻¹.

At the low temperatures of adiabatic pre-reforming, no cracking products are formed. Nevertheless, in the pre-reforming of higher hydrocarbons, benzene has been found as an intermediate product. Comparative experiments indicate that platinum lacks the activity to open aromatic rings, which could lead to significant amounts of aromatic by-products. But even on rhodium, which is more active in opening aromatic rings, benzene and toluene intermediates have been observed by some authors. Kinetic data is very limited for precious metal catalysts but successful fits of experimental have been made using power law and Langmuir-Hinshelwood type expressions.

Precious metals, compared to nickel catalysts, possibly offer a greater resistance against sulphur poisoning. At low temperatures, however, sulphur poisoning may still be severe. Nevertheless, recent experiments using bimetallic rhodium–nickel catalysts appear promising in terms of pre-reforming heavy feedstock with high sulphur content (22 ppm) at low temperature (< 520°C). Precious metals may also have advantages in terms of preventing carbon and/or coke formation. In contrast to nickel, catalysts based on platinum, rhodium, and ruthenium form little or no carbon filaments because the dissolution–precipitation mechanism cannot occur. These catalysts could therefore be applied at higher temperatures, which are beneficial for sulphur resistance and preventing gum formation. However, data on the occurrence or prevention of gum formation on precious metal catalysts is effectively lacking. Also lacking are data on the deactivation rates that may be expected over the lifetime of a precious metal pre-reforming catalyst.

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