

# **ON THE CATALYTIC ASPECTS OF STEAM-METHANE REFORMING**

**A Literature Survey**

**P. van Beurden**

# CONTENTS

LIST OF TABLES	3
LIST OF FIGURES	3
1. INTRODUCTION	4
1.1 Outline of the Report	4
1.2 Further Reading	4
2. CHEMISTRY OF STEAM-METHANE REFORMING	5
2.1 Thermodynamics	5
2.2 Reaction Rates and Kinetics	5
3. REFORMING CATALYSTS AND THE ROLE OF THE SUPPORT	7
3.1 Influence of Preparation and Activation Method on Catalytic Activity	7
3.2 The Active Metal	8
3.3 The Catalyst Support	9
3.3.1 Support Properties Influencing Catalysts	9
3.3.2 Support Participation in Catalytic Reactions	10
3.4 Reaction Mechanisms and Kinetic Details of Steam-Reforming	12
3.4.1 General Mechanisms for Steam-Methane Reforming	12
3.4.2 Specific Mechanisms Involving the Support	14
4. CATALYST DEACTIVATION AND PROMOTION	16
4.1 Catalyst Deactivation	16
4.1.1 Sintering	16
4.1.2 Oxidation	17
4.1.3 Sulfur Poisoning	17
4.1.4 Carbon Formation	17
4.2 Catalyst Promotion	19
5. NOVEL APPLICATIONS OF METHANE REFORMING	20
5.1 Sorption-Enhanced Reforming	20
5.2 Hydrogen Membrane Reactors	20
5.2.1 Catalytic Aspects of Membrane Reactors	21
5.2.2 Kinetic Aspects of Membrane Reactors	21
5.3 Reforming of Methane with CO <sub>2</sub>	22
6. PRESENT TRENDS IN REFORMING-CATALYST RESEARCH	23
6.1 Catalyst Preparation using Precursors	23
6.2 Alternative Supports	23
REFERENCES	25

## LIST OF TABLES

Table 3.1	<i>Relative activities for steam reforming of methane. <math>T=550^{\circ}\text{C}</math>, <math>S/C=4</math>, <math>P=1</math> bar (Rostrup-Nielsen, 1993)</i> .....	8
Table 4.1	<i>Routes to carbon formation</i> .....	18

## LIST OF FIGURES

Figure 3.1	<i>Mechanism of the water-gas shift reaction (2) on <math>\text{Pt/CeO}_2</math> (Swartz, 2003)</i> .....	11
Figure 3.2	<i>Schematic representation of the ceria assisted oxygen transport through the catalytic system</i> .....	14

## 1. INTRODUCTION

In the transition to sustainable energy hydrogen will play a key role as an energy carrier. Currently, hydrogen is most economically produced from fossil fuels. The most studied technology for hydrogen production from fossil fuels is *steam-methane reforming* (SMR), in which methane reacts with steam to produce a mixture of hydrogen, carbon dioxide, and carbon monoxide. In order to obtain acceptable reaction rates a catalyst is required to accelerate the process. Even more, the catalyst should be stable under the rather extreme conditions under which high CH<sub>4</sub> conversions can be reached (i.e., high temperatures and high probabilities of unwanted side reactions involving carbon deposition). This report deals with the catalytic aspects of the steam reforming of methane. More specifically, a review of selected, recent literature on catalyst research is presented and discussed. The purpose of this report is to provide the reader some insight in the many aspects of catalytic steam reforming and, ultimately, some support – a word of great significance as we will soon find out! – and guidance for the reader's own catalyst research.

### 1.1 Outline of the Report

The outline of this report is then as follows. In Chapter 2, the chemistry of methane-steam reforming is addressed, including the thermodynamics and reaction kinetics. Chapter 3 deals with the properties of reforming catalysts and is most probably the most important chapter of this report. Then, in Chapter 4, catalyst deactivation is discussed. Chapter 5 describes some applications of methane reforming other than the conventional steam reforming, including the reforming of methane with CO<sub>2</sub>. And finally, in Chapter 6, a selection of present trends in reforming catalyst research is discussed.

It should be noted here that the reforming of methane with CO<sub>2</sub> instead of H<sub>2</sub>O will often be used in discussions on catalyst properties throughout this report. This is justified, since these two processes are (chemically) highly related and involve similar catalysts and deactivation phenomena (Rostrup-Nielsen, 2002).

### 1.2 Further Reading

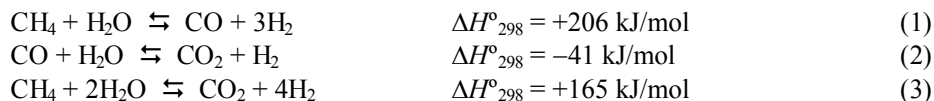
Several, more comprehensive, reviews have been written about reforming of methane. Classics are the books *Catalytic Steam Reforming* by Rostrup-Nielsen (Rostrup-Nielsen, 1984) and the *Catalyst Handbook* by Twigg (Twigg, 1989). An excellent review paper has recently been written by Rostrup-Nielsen, Sehested, and Nørskov (Rostrup-Nielsen, 2002): *Hydrogen and Synthesis Gas by Steam- and CO<sub>2</sub> Reforming*.

For a more general introduction to (heterogeneous) catalysis, the books by Somorjai (Somorjai, 1994), Thomas & Thomas (Thomas, 1967), Anderson & Pratt (Anderson, 1985), and Masel (Masel, 1996; Masel, 2001) are highly recommended.

## 2. CHEMISTRY OF STEAM-METHANE REFORMING

### 2.1 Thermodynamics

The steam reforming of methane consists of three reversible reactions: the strongly endothermic reforming reactions (1) and (3), and the moderately exothermic water-gas shift reaction (2):



It should be emphasized that  $\text{CO}_2$  is not only produced via the shift reaction (2), but also directly via the steam reforming reaction (3). This implies that reaction (3) is not just the 'overall reaction', despite the fact that in literature steam-methane reforming is often considered to be a combination of reactions (1) and (2) only.

Due to its endothermic character, reforming is favoured by high temperature. Also, because reforming is accompanied by a volume expansion, it is favoured by low pressure. In contrast, the exothermic shift reaction is favoured by low temperature, while unaffected by changes in pressure.

Increasing the amount of steam will enhance the  $\text{CH}_4$  conversion, but requires an additional amount of energy to produce the steam. In practice, steam-to-carbon ratios [i.e.,  $P(\text{H}_2\text{O})/P(\text{CH}_4)$ , or in short: S/C] around 3 are applied. This value for S/C will also suppress coke formation during the reaction, see also Section 4.1.4 and References (Rostrup-Nielsen, 1984; Rostrup-Nielsen, 1993; Rostrup-Nielsen, 2002).

In practice, the steam reforming process is divided in two sections: a section at high temperature and pressure<sup>1</sup> (typically 800–1000°C and 30–40 bar) in which the reforming and shift reactions (1–3) occur, followed by an additional (two step) shift-section at lower temperature (typically 200–400°C) in order to maximize the CO conversion via reaction (2). In such a process CO concentrations as low as 0.1% can be achieved.

### 2.2 Reaction Rates and Kinetics

Many studies have been performed to investigate the kinetics of steam reforming, and while there is general agreement on first order kinetics with respect to methane, the reported activation energies span a wide range of values. This might be explained by experimental inaccuracies due to transport restrictions in the sense of diffusion and heat transfer restrictions. The effect of diffusion limitation is exemplified by the work of Bodrov and co-workers, who found that the reaction rate of methane on a conventional nickel/alumina catalyst depends only on the partial pressure of methane, whereas on a nickel foil (having less diffusion restrictions) the rate depends also on the partial pressures of  $\text{H}_2\text{O}$ ,  $\text{H}_2$ , and CO (Bodrov, 1964; Bodrov, 1967).

Still, several accurate and reliable investigations have been performed, acknowledging the possibility of diffusional limitations. For instance, an extensive study of the intrinsic kinetics of the reforming and water-gas shift reactions on a  $\text{Ni/MgAl}_2\text{O}_4$ -spinel catalyst was performed by Xu and Froment (Xu, 1989). They developed a model, based on a Langmuir-Hinshelwood reaction mechanism, which includes as many as 13 reaction steps (see also Section 3.4.1).

---

<sup>1</sup> Although a high pressure negatively affects the  $\text{CH}_4$  conversion, it allows for more compact reactor design, which considerably reduces materials and heating costs.

Without going into details, in general, the rate equations of the steam reforming reactions (1–3) can be written as:

$$r_i = k_i f_i(P_x, K_x) / Z^2 (P_x, C_x); \quad i = 1, 2, 3; \quad x = \text{CH}_4, \text{H}_2\text{O}, \text{CO}_2, \text{CO}, \text{H}_2 \quad (4)$$

where the  $k_i$  denote the rate coefficients of the reactions  $i$ , which incorporate temperature dependence, adsorption enthalpies, reaction activation energies, and entropies. The  $f_i$  are complex functions of the partial pressures  $P_x$  and equilibrium constants  $K_i$ .  $Z$  is a function of  $P_x$  and the adsorption constants  $C_x$ . Reaction rates are typically expressed in mol/g<sub>cat</sub>/h. For example,  $r_1$ , the rate for reforming reaction (1), can be written as:

$$r_1 = k_1 \left( \frac{P_{\text{CH}_4} P_{\text{H}_2\text{O}}}{P_{\text{H}_2}^{2.5}} - \frac{P_{\text{H}_2}^{0.5} P_{\text{CO}}}{K_1} \right) / Z^2; \quad (5a)$$

$$Z = 1 + C_{\text{CO}} P_{\text{CO}} + C_{\text{H}_2} P_{\text{H}_2} + C_{\text{CH}_4} P_{\text{CH}_4} + C_{\text{H}_2\text{O}} \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}. \quad (5b)$$

The parameters included in the reaction rates of Eq. (4) can be derived from experiment by relating the conversions of the species to the space time (ratio of catalyst weight and gas flow,  $W/F$ ) of the species. For instance, the reaction rate for the disappearance of methane can be written as:

$$r_{\text{CH}_4} = r_1 + r_3 = \frac{d\chi_{\text{CH}_4}}{d(W_{\text{cat}} / F_{\text{CH}_4})}, \quad (6)$$

where  $r_1$  and  $r_3$  are the reaction rates for reactions (1) and (3), respectively,  $\chi$  denotes the conversion, and  $W/F$  is the space time. For further details, the reader is referred to Refs. (Xu, 1989) and (Rostrup-Nielsen, 1984).

From the above and other experimental studies, it is found that the shift reaction is very fast at reforming conditions. As a result, the water-gas shift equilibrium is always established during steam reforming.

### 3. REFORMING CATALYSTS AND THE ROLE OF THE SUPPORT

The higher the active surface area of the catalyst, the greater the number of product molecules produced per unit time. Therefore, much of the art and science of catalyst preparation deals with high-surface-area materials (typically 100–400 m<sup>2</sup>/g). These are prepared in such a way that they are often crystalline with well-defined microstructures and behave as active components of the catalyst system in spite of their accepted name 'supports'. The (transition) metal atoms are then deposited in the micropores, and the sample is subsequently heated and reduced to produce small metal particles, ideally 10–10<sup>2</sup> Å in size with virtually all the atoms located on the surface (i.e., unit dispersion<sup>2</sup>).

In this Section, catalyst preparation, the properties of the catalytically active metal, and the catalytic role of the support will be addressed. Although the headers of Sections 3.2 and 3.3 suggest differently, a clear distinction between 'catalytically active metal' and 'inactive support' can usually not be made and is therefore rather arbitrary. For it is often found that the 'support' plays an important role in the reaction steps involved with the catalytic process. For the sake of clarity, however, it may be useful to base a discussion of catalysts on such a distinction, but throughout this report their strong interplay will regularly be emphasized.

Finally, it should be noted that these topics are still the subject of investigation of many scientific studies and for several phenomena no unambiguous or conclusive theories have been established yet. Still, many of the properties of SR catalysts have been thoroughly studied and their specific behaviour is definitely understood at some (fundamental) level.

#### 3.1 Influence of Preparation and Activation Method on Catalytic Activity

Apart from the chemical composition, also physical properties relating to structure influence the reactivity and stability of catalysts. The preparation method determines these physical properties to a large extent. Although many preparation techniques are practiced, only two common methods will be addressed here.

Probably the most common technique for catalyst preparation is impregnation of a metal salt in an aqueous solution onto a support material, e.g.,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Another common method of catalyst preparation is co-precipitation. In this procedure, solutions of metal salts are added together, usually at constant pH, and precipitate into the desired product.

A general treatment after the synthesis is calcination (heating the sample in air, in order to 'clean up' and 'stabilize' the catalyst) and/or reduction (heating the sample in a reducing atmosphere, usually containing hydrogen, in order to activate the catalytic metal) of the catalyst.

The different effects of the impregnation and co-precipitation methods on the catalytic activity are illustrated by the following example. In our labs, two K-promoted catalysts have been prepared. One by impregnation and one by co-precipitation. Although the chemical compositions are basically identical, the addition of K completely deactivated the (initially active) impregnated catalyst for the steam-reforming reaction, whereas the addition of K to the co-precipitated catalyst did not severely affect the catalytic activity towards steam-reforming. Further, Wang and Lu investigated for nickel catalysts the effects of support phase and preparation technique on the reforming of methane with CO<sub>2</sub> (i.e., dry reforming, see Section

---

<sup>2</sup> The dispersion of a particle is the ratio of the number of surface atoms to the total number of atoms. A high dispersion generally corresponds to a small particle size.

5.3) (Wang, 1998b). They found, amongst others, that the impregnated Ni/MgO-catalyst performed better than the co-precipitated one (this is, however, definitely not a general result).

It should be noted here that also the metal precursor used to impregnate the support, as well as the calcination and reduction procedures (i.e., temperature, time, and gas composition) strongly affect the catalytic properties of the prepared catalyst. For instance, Wang and Lu also studied the effect of the nickel precursor on the activity of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts for the dry reforming of methane (Wang, 1998c). They concluded that catalysts derived from inorganic precursors (e.g., nickel nitrate) are more active and stable than organic-derived precursors. Also, Matsumura *et al.* (Matsumura, 2004) found that Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is not very active for steam reforming when reduced at 500°C. Only after reduction at 700°C, Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> will be fairly active. Similar results concerning the reduction procedure were found by Wang and Lu in yet another study on the dry reforming of methane with Ni/MgO catalysts (Wang, 1998a). They ascribe this effect to the fact that a solid-solution of NiO and MgO exists, which is more difficult to activate.

Therefore, identifying a catalyst on the basis of its chemical composition only (e.g., 15wt% Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), does not provide much information about its stability or activity. In fact, turnover-frequencies<sup>3</sup> may differ several orders of magnitude for catalysts which are “the same” in terms of chemical composition. This might explain the fact that the many orders of catalyst activity reported in literature are not always consistent [see, e.g., Ref. (Wang, 1996) and cf. with Ref. (Yokota, 2002)]. Consequently, a study of the influence of the preparation procedure on the catalyst performance should be a central part of all catalyst research.

### 3.2 The Active Metal

For steam-reforming, usually Ni or the noble metals Ru, Rh, Pd, Ir, Pt are used as the active metal in catalysts. Because of its low costs, Ni is the most widely used metal from this set. Ni, however, is less active (Table 3.1) and usually more prone to deactivation by, e.g., carbon formation or oxidation (see also Chapter 4).

Table 3.1 *Relative activities for steam reforming of methane. T=550°C, S/C=4, P=1 bar (Rostrup-Nielsen, 1993)*

Catalyst metal content (wt%)	Relative rate
Ni (16)	1.0
Ru (1.4)	2.1
Rh (1.1)	1.9
Pd (1.2)	0.4
Ir (0.9)	1.1
Pt (0.9)	0.5

The activity of a catalyst is related to the metal surface area (i.e., the number of active sites). This implies that, generally, the catalytic activity benefits from a high dispersion of the metal particles. Common dispersions for Ni catalysts are of 2–5%, with metal particles of 20–50 nm (Rostrup-Nielsen, 1984). There is an optimum beyond which an increase in Ni-content does not produce any increase in activity, usually around 15–20 wt% (depending on support structure and surface). Although the nickel surface area is generally increased with higher loadings, the dispersion or utilization of the nickel tends to decrease with increasing nickel content. Hence, the activity will not increase any further.

<sup>3</sup> The turnover-frequency (TOF) is the number of product molecules formed per second. The specific turnover-rate is the TOF divided by the catalyst surface area. In literature, the specific turnover-rate is also often called turnover-frequency.



Apart from the amount of available metal surface area, also the structure of the available surface area strongly influences the catalyst activity. For instance, the close-packed (111) surface of nickel is less active than the more open (110) surface. In fact, metal atoms in surface steps and near defects are much more reactive than metal atoms in the higher coordinated surface terrace sites. For instance, it is known that Ni particles are composed of a number of single crystals (i.e., the metal particles are polycrystalline) (Sehested, 2001), which, however, are not completely 'space filling'. Therefore, some lattice distortion is required and these dislocations are expected to play a role in the catalytic reaction (Smith, 1981). This agrees with the conclusions of Wei and Iglesia (Wei, 2004), who investigated the catalytic activity of catalysts with different loadings of Rh on  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  supports. They found that  $\text{CH}_4$  reforming turnover rates increased as the size of Rh clusters decreased, suggesting that coordinatively unsaturated Rh surface atoms prevalent in smaller clusters activate C–H bonds more effectively than atoms on lower-index surfaces. This is confirmed by the results of the theoretical studies performed by Nørskov and co-workers (Bengard, 2002; Rostrup-Nielsen, 2002), which indicate that steps are much more reactive than the close-packed surface. They also investigated the negative effect of K on the activity of Ni-catalysts. They found that K blocks sites at step edges, thereby inhibiting the role of steps in the reaction process.

In contrast with the discussion above, however, it was concluded by Rostrup-Nielsen *et al.* [Ref. (Rostrup-Nielsen, 1984) and references therein] that the activity per unit metal surface area (the specific activity) *decreases* with increasing dispersion (i.e., with smaller metal crystal size). This effect may be explained by a decrease of large ensemble landing sites (Frennet, 1978) on the smaller particles (i.e., an entropy-effect). Alternatively, it may be explained in terms of a change in electronic state of the metal particles: Yokota and co-workers (Yokota, 2002) showed for Rh-based catalysts that a higher dispersion may result in a less metallic – and hence less reactive – character of the Rh particles. Still, the reasons for these discrepancies remain unclear.

The synergism between different metals has also been investigated. For instance, Rh-promoted Ni/ $\alpha$ - $\text{Al}_2\text{O}_3$  was found to possess higher activity than either Ni/ $\alpha$ - $\text{Al}_2\text{O}_3$  or Rh/ $\alpha$ - $\text{Al}_2\text{O}_3$  catalysts in the methane reforming with  $\text{CO}_2$  (Hou, 2003). In this case, Rh improved the dispersion of Ni, retarded the sintering of Ni, and increased the activation of  $\text{CO}_2$  and  $\text{CH}_4$ .

### 3.3 The Catalyst Support

The influence of the support on the steam-reforming reaction can hardly be overrated. It not only determines the dispersion of the catalytically active metal particles or the catalyst's resistance to sintering, it also affects the reactivity and coke resistance of the metal particles, and may even participate in the catalytic reaction itself. In other words, the support is a fundamental part of the catalyst and cannot be considered separately.

#### 3.3.1 Support Properties Influencing Catalysts

In first instance, the role of the support is – literally – to provide a support for the catalytically active metal, in order to obtain a stable and high active surface area. Among the most common supports for methane reforming are  $\alpha$ - and  $\gamma$ - $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{MgAl}_2\text{O}_4$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ , and  $\text{TiO}_2$ . These supports have good porosity, which results in a long contact-time between reactants and catalyst. Maintaining a high active surface area is also important: the support can affect the migration and coalescence of metal particles (i.e., sintering, see Section 4.1.1) in various ways. Pore structure, morphology, and phase transitions of the support determine the final particle size of the metal.

But there is more. Obviously, due to the nature of the chemical bonding between the support and the metal atoms, the electronic properties – and hence the reactivity – of the metal is affected. For instance, acidity in the support is known to facilitate the decomposition of methane, but it will also promote cracking and polymerization, producing carbon. In general, a

strong interaction between metal and support makes a catalyst more resistant to sintering and coking, thus resulting in a longer time of catalyst stability (Wang, 1998b).

Bradford *et al.* (Bradford, 1996) found for Ni/MgO catalysts that formation of a partially reducible NiO–MgO solid solution appeared to stabilize surface Ni–Ni bonds and prevent carbon diffusion into nickel particles. They suggest that indeed the support influences the catalyst activity by altering the electron donating ability of the reduced nickel surfaces. In addition they found that a strong metal-support interaction emerges for Ni/TiO<sub>2</sub> catalysts which leads to blockage of the active nickel sites due to migration of TiO<sub>x</sub>-species from the TiO<sub>2</sub>-carrier (Zhang, 1996; Bradford, 1996; Takatani, 1984). Partly as a result of this site blocking, carbon formation is drastically reduced on Ni/TiO<sub>2</sub>. In contrast, it was concluded that a lack of metal-support interaction in Ni/SiO<sub>2</sub> permitted substantial formation of filamentous whisker carbon.

The effect of the support on the electronic properties of the catalytically active metal is also illustrated by Yokota and co-workers (Yokota, 2002). They found that 0.5 wt% Rh on SiO<sub>2</sub> is more active than 0.5 wt% Rh on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for the CH<sub>4</sub> reforming reaction with CO<sub>2</sub> at 700°C, despite the higher dispersion of Rh on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. This seemingly contradictory result is probably caused by the fact that a stronger metal-support interaction exists for Rh on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Accordingly, the Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> system tends to maximize its number of metal-support bonds, resulting in a higher dispersion. Then, as a consequence of this stronger metal-support interaction, Rh loses its metallic character (i.e., electrons are withdrawn from Rh) and because of that, Rh possesses a rather cationic character on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, resulting in the formation of less reactive Rh<sub>2</sub>O<sub>3</sub>-like structures<sup>4</sup>.

For *amorphous* CeO<sub>2</sub> as a support for Pd catalysts, a strong metal-support interaction leads to partial encapsulation of Pd particles, resulting in significantly reduced catalytic activity for steam reforming (Craciun, 2002). For more complex supports, synergetic effects can emerge. For instance, Ni supported on MgO–CaO showed high basicity and lower coke forming ability, attributed to the addition of CaO (Yamazaki, 1992). Al<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> is known for its catalytic stability and coking resistance, whereas CeO<sub>2</sub> itself may lead to significantly reduced catalytic activity (Wang, 1998a). In the case of the combined Al<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> support, the beneficial effects (i.e., high porosity and increased stability) of both supports are utilized (Craciun, 2002; Wang, 1998d) – at least, when crystalline (i.e., oxidized) instead of amorphous (i.e., reduced) CeO<sub>2</sub> is used, as mentioned above. In fact, CeO<sub>2</sub> is actually contributing the reaction mechanism itself. The role of CeO<sub>2</sub> and similar catalytically active supports will be discussed next.

### 3.3.2 Support Participation in Catalytic Reactions

In addition to the effects of the support on catalytic activity as discussed in the previous Section, the support may also actively participate in the catalytic reaction itself. For instance, supports with a basic nature, such as MgO, are known to enhance the activation of steam (i.e., dissociation into reactive OH and H species). Also, stabilization of different CH<sub>x</sub>-intermediates contributes to the overall reaction mechanism.

An important factor for catalyst reactivity and stability lies in the catalyst's resistance to carbon deposits, which could lead to active site blocking. Apart from directly altering the metal's properties by additives (see Section 4.2), an alternative route is to use a support which suppresses carbon deposition. This can be achieved with so-called oxy-transporters, such as ZrO<sub>2</sub> or CeO<sub>2</sub>, which are capable of oxidizing deposited carbon. Additionally, because of their oxygen conducting properties, these supports can actively participate in the catalytic reaction by

<sup>4</sup> Here also contradictory results appear in literature: Wei and Iglesia claim that the support does not influence the turnover frequency of methane activation for Rh/Al<sub>2</sub>O<sub>3</sub> and Rh/ZrO<sub>2</sub> catalysts in the CO<sub>2</sub> and H<sub>2</sub>O reforming of methane (Wei, 2004).

oxidizing or reducing reaction intermediates. As an example, the role of  $\text{CeO}_2$  in the water-gas shift reaction (2) is shown in Figure 3.1. The oxygen transport properties of  $\text{CeO}_2$  and their involvement in the WGS reaction are clearly illustrated. Also, the synergism between Pt and  $\text{CeO}_2$  is apparent: while Pt activates CO,  $\text{CeO}_2$  activates  $\text{H}_2\text{O}$  and provides the required oxygen for the oxidation of CO.

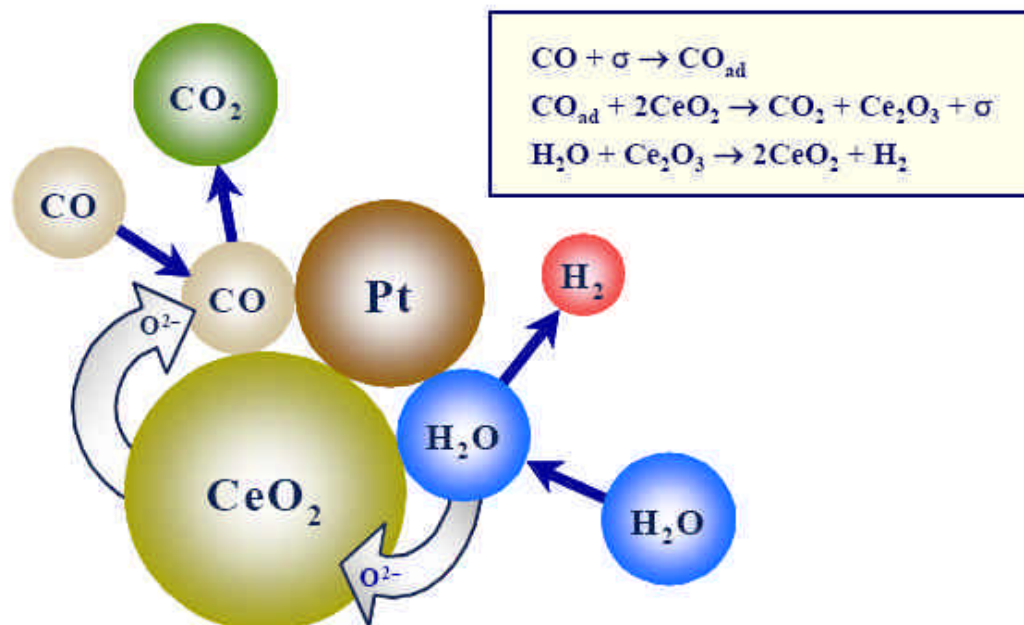


Figure 3.1 Mechanism of the water-gas shift reaction (2) on Pt/ $\text{CeO}_2$  (Swartz, 2003)

The role of ceria-containing supports has attracted a lot of attention in recent catalyst research. Especially  $\text{CeO}_2\text{-Al}_2\text{O}_3$ ,  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ , and  $\text{CeZrO}_x\text{-Al}_2\text{O}_3$  supports are extensively investigated. For instance, Dong and co-workers investigated methane reforming over  $\text{Ni/Ce}_{0.15}\text{Zr}_{0.85}\text{O}_2$  catalysts (Dong, 2002). They concluded that two kinds of active sites exist, one for methane activation (on Ni) and one for steam or oxygen activation (on the  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ -support). This is in line with the mechanism for WGS shown in Figure 3.1: Due to the addition of ceria, the ability to store, release, and transfer oxygen species is acquired, resulting in an enhanced ability to prevent carbon formation that would normally accumulate on the metal or metal-support interface.

They also found that part of the Ni (NiO) incorporates in the surface of the  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ -support and the resulting strong interaction between NiO and the  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  matrix inhibits the reduction of NiO. This is in agreement with the results of Craciun *et al.* (Craciun, 2002) who found that Pd is partly encapsulated in amorphous  $\text{CeO}_2$  on  $\gamma\text{-Al}_2\text{O}_3$ . Nonetheless, on crystalline  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ , Pd is found to be well dispersed and fairly active. This suggests that the crystallographic structure plays an important role in the reactivity of the support and catalyst as well. The results of Roh *et al.* (Roh, 2004) exemplify this idea, as they found that co-precipitated Ni-Ce-Zr $\text{O}_2$  catalysts are most active for  $\text{CH}_4\text{-CO}_2$  reforming when they have cubic phase ( $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ ), instead of tetragonal phase ( $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$ ) or mixed phase ( $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ ).

The specific effect of the addition of ceria to  $\text{ZrO}_2$  was demonstrated by Noronha *et al.* (Noronha, 2003) for methane reforming with different feed-gas compositions and pressures at  $800^\circ\text{C}$ . It was concluded that the overall increased stability of  $\text{Pt/Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$  with respect to

Pt/ZrO<sub>2</sub> could be ascribed to the higher density of oxygen vacancies on the support, which favours the 'carbon-cleaning mechanism' of the metal particle. This was illustrated by the fact that the addition of H<sub>2</sub>O strongly decreased the CH<sub>4</sub> and CO<sub>2</sub> conversion during the reaction on Pt/ZrO<sub>2</sub>, as a consequence of an increased amount of carbon deposition. This lower stability of the Pt/ZrO<sub>2</sub> catalyst was ascribed to the oxidation and decrease of the amount of oxygen vacancies by water, inhibiting oxygen transport and therefore the cleaning mechanism. On the other hand, Pt/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> was quite stable in the presence of water. This stability was ascribed to the higher amount of oxygen vacancies on the ceria-promoted support. Both catalysts, however, deactivated quickly during CO<sub>2</sub> reforming of methane under pressure of 13 barg, due to – again – carbon deposition. This is explained by the fact that under high pressure the rate of methane decomposition on Pt becomes higher than the rate of oxygen transfer of the support. Ergo, the activity of the metal is definitely not the only important parameter in overall catalyst activity and stability.

Another intriguing example of active involvement of the support during the reforming of CH<sub>4</sub> is observed by Zhang and Verykios (Zhang, 1996; Verykios, 2003). They reported that the Ni/La<sub>2</sub>O<sub>3</sub> catalyst showed high stability during the reaction of CH<sub>4</sub> with CO<sub>2</sub>, because an alternate reaction pathway occurred at the Ni/La<sub>2</sub>O<sub>3</sub> interface. They proposed a mechanism in which CH<sub>4</sub> mainly cracks on the Ni crystallites to form H<sub>2</sub> and surface carbon species (CH<sub>x</sub>), while CO<sub>2</sub> preferably adsorbs on the La<sub>2</sub>O<sub>3</sub> support to form La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> species. The nickel particles are partially covered by these La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> species, which participate directly in reactions with surface carbon species on the neighbouring Ni sites to form CO. Due to the existence of such synergetic sites which consist of Ni and La elements, the deposited carbon on the Ni sites is favourably removed by the oxycarbonate species originating from La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, thus resulting in an active and stable performance.

### 3.4 Reaction Mechanisms and Kinetic Details of Steam-Reforming

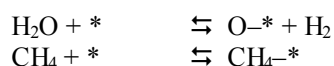
The reaction mechanism of the steam-reforming process strongly depends on the catalyst, i.e., on the catalytically active metal *and* the nature of the support. Hence, the outline of this Section is as follows: In Section 3.4.1, 'conventional' reaction mechanisms will be discussed on 'standard' catalysts. This will provide insight into typical reaction steps and rate limiting steps. In Section 3.4.2, reaction mechanisms involving catalysts with 'active supports' will be addressed, in order to emphasize the active role of the support and the research interest for this type of catalysts in general.

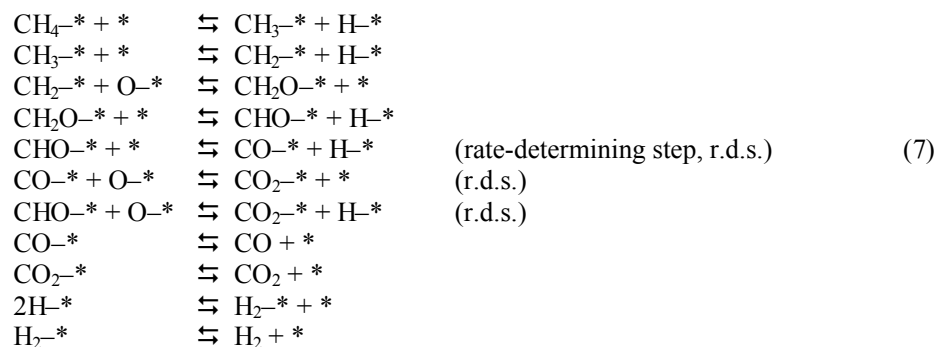
#### 3.4.1 General Mechanisms for Steam-Methane Reforming

As mentioned in Chapter 2, Xu and Froment (Xu, 1989) extensively studied the kinetic and mechanistic details of steam-methane reforming on a Ni/MgAl<sub>2</sub>O<sub>4</sub> catalyst. They arrived at the following reaction mechanism:

1. H<sub>2</sub>O reacts with surface nickel atoms, yielding adsorbed oxygen and gaseous hydrogen.
2. The H<sub>2</sub> formed is directly released into the gas phase and/or the gaseous H<sub>2</sub> is in equilibrium with adsorbed H and H<sub>2</sub>.
3. Methane is adsorbed on surface nickel atoms. The adsorbed methane either reacts with the adsorbed oxygen or dissociates to form chemisorbed radicals, CH<sub>x</sub> with  $x = 0-3$ .
4. The adsorbed oxygen and the carbon-containing radicals react to form chemisorbed CH<sub>2</sub>O, CHO, CO, or CO<sub>2</sub>.
5. CO and CO<sub>2</sub> are formed out of CHO and CH<sub>2</sub>O species.

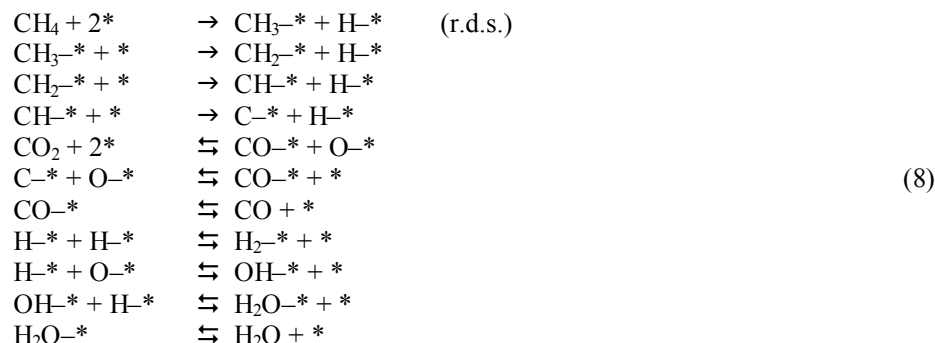
This results in the following reaction scheme ('\*' denotes a surface site):





This model nicely illustrates the many possible steps involved in the steam reforming of methane. It should be noted, however, that Rostrup-Nielsen *et al.* (Rostrup-Nielsen, 2002) argue that the model by Xu and Froment is not consistent with the current understanding of methane dissociation, which has been shown not to proceed via an adsorbed precursor state (Nielsen, 1995).

Wei and Iglesia (Wei, 2004) investigated the mechanisms for the reactions of CH<sub>4</sub> with CO<sub>2</sub> and H<sub>2</sub>O on Rh clusters. Interestingly, they found that reaction rates were proportional to CH<sub>4</sub> partial pressure, but independent of CO<sub>2</sub> and H<sub>2</sub>O pressures, which leads to the conclusion of sole kinetic relevance of C–H bond activation steps. Their data indicate that co-reactant (CO<sub>2</sub> or H<sub>2</sub>O) activation and its kinetic coupling with CH<sub>4</sub> activation via scavenging of chemisorbed carbon intermediates are fast steps and lead to Rh surfaces essentially uncovered by reactive intermediates. It was also shown that C–H bond activation elementary steps are irreversible and that recombinative desorption steps of H atoms with OH groups to form H<sub>2</sub> or H<sub>2</sub>O are quasi-equilibrated. The quasi-equilibrated nature of these and other steps confirms that water-gas shift reaction (2) is also at equilibrium. And remarkably, any involvement of the support in the activation of co-reactants was found not to be kinetically relevant. They then arrive at the following mechanism for CH<sub>4</sub> activation:



When ‘\*’ is the most abundant surface intermediate, it is found that only the rate constant for the CH<sub>4</sub> + 2\* → CH<sub>3</sub>–\* + H–\* reaction appears in the rate expression and the overall CH<sub>4</sub> conversion rates become proportional to CH<sub>4</sub> concentration and independent of the identity or concentration of co-reactants.

Note the fundamental difference in rate determining steps between Eqs. (7) and (8). The first mechanism indicates that reactions of carbon-intermediates with adsorbed oxygen are rate determining, suggesting that the properties of the oxygen present may determine to a large extent the reaction kinetics. This again emphasizes the possible importance of a oxygen-conducting support, such as ceria. On the other hand, the second mechanism indicates that the reactivity of the metal towards C–H bond breaking governs the overall reaction kinetics. This

emphasizes the importance of the catalytic activity of the metal. In general, a well-balanced interplay between the metal and support will undoubtedly lead to the best catalytic performance.

In my opinion, the mechanism represented by Eq. (8) is more realistic. For one reason, it is generally accepted among experimentalists and theoreticians that the activation of methane is a (or *the*) rate determining step. Another reason is that Xu and Froment find an unlikely negative heat of adsorption of steam, which is not a strong argument in favour of their mechanism either.

### 3.4.2 Specific Mechanisms Involving the Support

The active role of the support in the reforming of methane is analysed by Kurungot and Yamaguchi (Kurungot, 2004) for  $\text{CeO}_2$ -doped  $\text{Rh}/\gamma\text{-Al}_2\text{O}_3$ . They suggest that the improved catalyst performance was achieved by the kinetic and oxidative stabilization of the catalyst matrix with  $\text{CeO}_2$ . As a possible mechanism, they put forward the following scheme, based on a Mars-van Krevelen redox cycle, Figure 3.2.

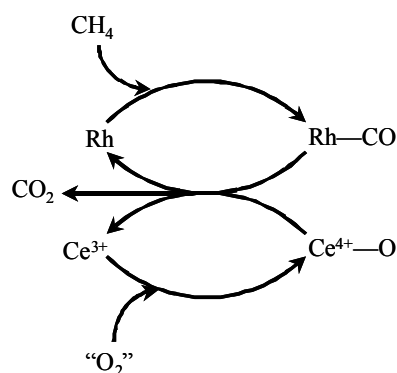


Figure 3.2 Schematic representation of the ceria assisted oxygen transport through the catalytic system

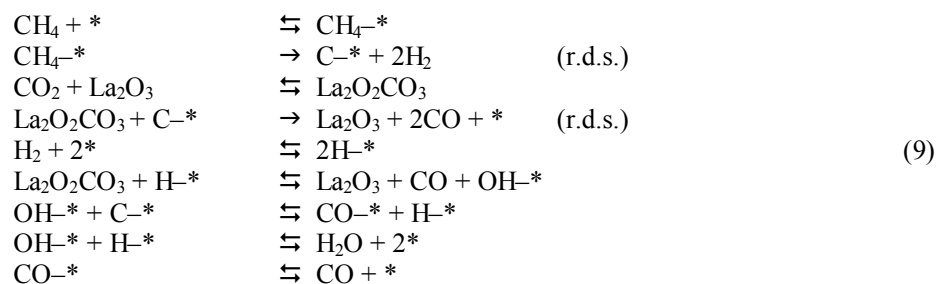
Here, the adsorbed methane reduces the metal oxide, which gets reoxidised by the oxygen from the feed. The rate of  $\text{CH}_4$  adsorption will be significantly reduced unless the oxygen loss is replenished in the process. Ceria can accelerate the oxygen transport properties of the system due to its ability to store and release oxygen. This property of ceria originates from the fact that both  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  are stable, allowing the oxide to shift between  $\text{CeO}_2$  and  $\text{CeO}_{2-x}$ . The lattice oxygen released during ceria reduction can react with  $\text{CH}_4$  and  $\text{CO}$  under rich conditions. The redox cycle assisted by the oxygen-buffering effect of ceria is represented in Figure 3.2.

A similar mechanism for  $\text{Ni}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  is described by Dong *et al.* [Ref. (Dong, 2002) and references therein]. It is reported that  $\text{CeO}_x$  enhances the dissociation of  $\text{H}_2\text{O}$  and accelerates the reaction of steam with adsorbed species on the nickel surface near the boundary area between metal and support, thus decreasing the carbon deposition and promoting the stability of the catalyst during reforming. Therefore, it was suggested that both the metal and the support play important roles in the oxy-steam-methane reforming (OSMR). In their proposed mechanism,  $\text{CH}_4$  dissociates on the metallic nickel surface, while both  $\text{H}_2\text{O}$  and  $\text{O}_2$  competitively adsorb on nickel and the  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  support, similar to the scheme in Figure 3.2. It is assumed that the catalyst surface is mostly occupied by C,  $\text{CH}_x$ , O, and OH. They conclude that the high activity and stability of 15wt% Ni on  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  are mainly due to a good balance between two kinds of active sites, i.e., one for the activation of methane and the other for that of steam or oxygen.

Verykios *et al.* studied the dry reforming of methane on  $\text{La}_2\text{O}_3$ -supported Ni catalysts (Zhang, 1996; Verykios, 2003). They put forward the following mechanism:

1. Reversible adsorption of methane on the surface of Ni, leading to cracking of methane and production of carbon deposits and hydrogen;
2. A strong interaction exists between CO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> exists, which leads to the formation of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> species;
3. La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> species react with carbon deposited onto Ni particles at the interface between Ni and La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>. In this way the CH<sub>4</sub> cracking activity of Ni is restored and the catalyst exhibits good stability. Therefore, the active portion of the catalyst is the interfacial area between Ni and oxycarbonate particles. The remaining surface of Ni is covered by carbon deposits;
4. Adsorbed hydrogen, at very low surface coverage, may also exist and interact with other surface species. This adsorbed hydrogen originates from the sequential cracking of CH<sub>4</sub>.

This leads to the following reaction scheme:



Just as discussed earlier (Section 3.4.1), the first reaction step in (9) is questionable. Apart from this first step, however, the overall mechanism seems definitely credible.

## 4. CATALYST DEACTIVATION AND PROMOTION

### 4.1 Catalyst Deactivation

There can be many reasons for catalyst deactivation. Understanding the causes of deactivation and developing new catalysts that are more resistant to poisoning are constant concerns of the catalytic chemist. It should be mentioned here that a distinction between poisoning and thermal deactivation can be made: If, on continued use, the activity decreases more rapidly than surface area, then poisoning may be suspected, whereas, if as decrease in surface area is concomitant with a decrease in activity, then thermal deactivation is indicated. The latter is for instance the case with *sintering*, which will be discussed in the next Section.

#### 4.1.1 Sintering

Sintering is the process of agglomeration of the crystallites of the active phase, which leads to loss of active surface and, consequently, a decrease in activity. Apart from reduced dispersion, also ideally shaped crystallites are formed, which are generally less reactive. According to the Rule of Tammann, sintering is generally to be expected at temperatures above  $0.5T_m$ , where  $T_m$  is the melting temperature of the metal in Kelvin. Surface diffusion is already expected to occur above  $0.33T_m$  (Hüttig Temperature).

The actual rate and extent of sintering depends on many factors, including the metal concerned, the metal content, initial crystallite size and size distribution, the dispersion of the metal across the support, the nature of the support material and the operating conditions. The most important factors are the temperature and the atmosphere in contact with the catalyst: elevated temperatures and the presence of water significantly enhance sintering. Also, sintering tends to be faster for narrow particle size distributions on the support. It has been proposed that the pore structure, morphology, and phase transitions of the support determine the final particle size of the metal.

In most catalytic processes the temperatures and the size of the metal crystallites are such that, without the presence of a support, extensive agglomeration would occur in seconds. The effectiveness of the support in hindering metal movement and the movement of the support itself, factors controlled primarily by catalyst formulation, are thus of great importance.

The aggregation of metal particles necessarily involves the transport of metal within the catalyst, although it is often difficult to determine whether this occurs by the migration of metal atoms (Ostwald ripening) or by crystallite migration and coalescence. Alternatively, sintering may occur by atoms through the gas phase (usually promoted by poisons or reactants which form compounds with the metal).

For both of these surface migration processes, the driving force for sintering is the difference in particle surface energy, which varies inversely with particle size. In both processes, sintering slows down with time and results in a semi-stable state, with characteristic particle size distributions.

Most studies of sintering indicate that the particle migration and coalescence is the preferred process over atom migration, although experiments suggest that at higher temperatures atom migration becomes more dominant [see also Ref. (Rostrup-Nielsen, 2002) and references therein].



#### 4.1.2 Oxidation

Oxidation of the metal particles may occur at a high steam-to-carbon ratio and a low catalyst activity. Especially nickel catalysts are prone to oxidation. Since the catalytically active phase is the metallic phase, oxidation leads to deactivation of the catalyst. Usually, nickel catalysts are activated by reducing with a hydrogen-rich gas, prior to steam-reforming operation. Noble metal catalysts are generally not sensitive to oxidation.

Preferential oxidation of (poor) Ni catalysts readily occurs at low temperatures (say, below 500°C) and has under these conditions an even stronger deactivating effect than carbon formation (Matsumura, 2004; Ayabe, 2003). This can be understood if one realizes that, at low temperatures, CH<sub>4</sub> conversion is low and hence, the (oxidizing) H<sub>2</sub>O concentration is high and the (reducing) H<sub>2</sub> concentration is low. Under 'regular' steam-reforming conditions though, sufficient hydrogen will be present to keep most of the active nickel surface reduced.

#### 4.1.3 Sulfur Poisoning

Many of the catalyst poisons act by blocking active surface sites. In addition, poisons may change the atomic surface structure in a way that reduces the catalytic activity. Sulfur is the most severe poison for steam reforming catalysts. The sensitivity of the reforming catalyst to poisoning increases at lower operating temperatures. So, while poisoning of the (nickel) catalyst occurs with about 5 ppm of sulfur in the feed gas at a temperature of 800°C, concentrations of the order of 0.01 ppm poison the catalyst already at 500°C. This can be understood if one realizes that the poisoning process can be represented by a simple exothermic adsorption process. It is known that sulfur actually changes the surface structure of nickel (adsorbate-induced surface reconstruction) (Somorjai, 1972).

Sulfur is, under reforming conditions, present in the form of H<sub>2</sub>S, which is chemisorbed on transition-metal surfaces:



In principle, it is possible to regenerate the poisoned catalyst by treatment with hydrogen [the reverse of reaction (10)], but the driving force is extremely small. Alternatively, sulfur may be removed by oxidation and controlled re-reduction of the catalyst.

#### 4.1.4 Carbon Formation

At the operating temperatures some of the reactant CH<sub>x</sub>-species may completely decompose and deposit a thick layer of inactive carbon on the catalyst surface (coke). Especially with nickel-based catalysts, steam reforming involves the risk of carbon formation, which may cause serious operational problems and catalyst deactivation. Generally, higher hydrocarbons are more prone to carbon formation than methane. This is related to the fact that for higher hydrocarbons the initial surface carbon intermediates are more readily formed. The concentration of these intermediates is an important factor, and is critical in influencing the delicate balance between carbon-forming and carbon-removing reactions.

On nickel surfaces, carbon formation may take place mainly by three routes (Rostrup-Nielsen, 1984; Rostrup-Nielsen, 2002), as summarized in Table 4.1.

At lower temperatures (say 500°C and below), adsorbed hydrocarbons may accumulate on the surface and slowly be transformed into a non-reactive polymer film ('gum') blocking and deactivating the surface. This phenomenon can be retarded by hydrogen. Note that because of the endothermic nature of the steam-reforming reaction, high catalyst activity leads to a low temperature at the reaction site, resulting in a higher risk for carbon formation.

At higher temperatures, whisker carbon is the principal product of carbon formation on nickel catalysts. The underlying mechanism is quite comprehensive, it involves diffusion of carbon atoms through the metal particles. For details, see Ref. (Rostrup-Nielsen, 1984).

The rate of carbon formation was found to be far less on noble metals than on nickel (Rostrup-Nielsen, 1993). This result may be explained by the fact that the noble metals do not dissolve carbon. The carbon formed on the noble metals was observed to be of a structure that was difficult to distinguish from the catalyst structure.

Table 4.1 *Routes to carbon formation*

Carbon type	Reactions involved	Phenomena	Critical parameters
Gum	$C_nH_m \rightarrow (CH_2)_n \rightarrow \text{gum}$	Blocking of surface by polymerisation of adsorbed $C_nH_m$ radicals: progressive deactivation	Low S/C ratio, absence of $H_2$ , low temperature (below $\sim 500^\circ\text{C}$ ), presence of aromatics
Whisker carbon, amorphous carbon	$CH_4 \rightarrow C + 2H_2$ $2CO \rightarrow C + CO_2$ $CO + H_2 \rightarrow C + H_2O$ $C_nH_m \rightarrow nC + m/2H_2$	Break-up of catalyst pellet (whisker carbon: <i>no</i> deactivation of the surface)	Low S/C ratio, high temperature (above $\sim 450^\circ\text{C}$ ), presence of olefins, aromatics
Pyrolytic coke	$C_nH_m \rightarrow \text{olefins} \rightarrow \text{coke}$	Encapsulation of catalyst pellet (deactivation), deposits on tube wall	High temperature (above $\sim 600^\circ\text{C}$ ), high residence time, presence of olefins, sulfur poisoning

The carbon formation depends on the kinetic balance between the surface reaction of the adsorbed hydrocarbons with oxygen species and the further dissociation of the hydrocarbon into adsorbed carbon atoms.

For a given hydrocarbon feed, temperature and pressure, carbon will be formed below a critical steam-to-carbon ratio (S/C) (Twigg, 1989; Rostrup-Nielsen, 2002). This critical S/C ratio increases with temperature and is dictated by thermodynamics. In practice however, carbon formation generally occurs before the thermodynamic limit is reached (e.g., by poisons, temperature and concentration gradients, etc.). By promotion of the catalyst (see also Section 4.2), it is possible to push the carbon formation limit to the thermodynamic limit. For instance, Haldor Topsøe A/S developed a process (SPARG) in which by 'controlled passivation' of the catalyst surface by sulfur, carbon deposition is inhibited (Udengaard, 1992). By using noble metal catalysts, it is possible to push the carbon limit even beyond the thermodynamic limit.

As already indicated in Table 4.1, not all carbon formation necessarily leads to catalyst deactivation. It is the nature of the deposited carbon that determines to what extent the catalytic activity will be affected. For instance, for dry reforming of methane it is shown that the relative ease with which carbon is removed (oxidized) from the surface affects the catalytic activity more than the actual amount of carbon that is present on the catalyst surface (Wang, 1998a). It was concluded that graphitic carbon is more reactive than amorphous carbon, which in turn causes the varying catalytic activity and stability of the catalyst. This is consistent with Table 4.1: 'Whisker carbon', which does not necessarily lead to deactivation, is known to be graphitic (Rostrup-Nielsen, 1984).

## 4.2 Catalyst Promotion

A promoter may increase the surface area available for adsorption and reaction, it may inhibit unwanted side reactions to occur, or it may increase the catalyst activity per unit surface area. In the latter case, promoters are usually electron donors (alkali metals) or electron acceptors (halogens), which act as bonding modifiers for adsorbed reactants<sup>5</sup>.

In the case of methane reforming, the purpose of a promoter is usually to inhibit carbon deposition on the active metal. In practice, suppression of carbon formation on (Ni-based) catalysts is usually achieved by adding small amounts of an alkali metal to the catalyst. As discussed in Section 3.3.1, acidic supports will promote cracking of methane, and thus producing carbon. Introducing basicity into the catalyst by addition of alkali metals will therefore suppress carbon formation. A different point of view to the promoting effect of alkali metals is given by Bengaard *et al.* (Bengaard, 2002). Their theoretical studies using density-functional theory (DFT) indicated that on Ni surfaces, potassium forms rows with oxygen along steps. Based on these results, it was suggested that the major carbon-preventing effect of these promoters is to block the steps and hence remove the nucleation sites for graphite formation. In this case, addition of promoters decrease the activity of the catalyst (Rostrup-Nielsen, 2002). The decrease should be determined by the promoter coverage at steps. The promoters need not cover all step sites to prevent carbon (graphene) nucleation, because a graphene island of a certain finite size is needed for it to be stable. Promotion can therefore hamper graphite formation without destroying the activity completely. As an alternative to K, it was suggested to promote the catalyst with Au. The decoration of steps with gold would be more effective, because Au will spread out along the step, whereas the interaction of potassium with oxygen leads to attractive interactions between the potassium atoms. The addition of less than almost complete step coverage will lead to a fraction of the steps being completely covered while the rest are free and open for reaction. This implies that promotion will decrease activity, but the activation energy should be unaltered because the nature of the active site does not change.

Additives other than alkali metals which suppress carbon formation on nickel catalysts are also reported, e.g., MoO<sub>3</sub> (Borowiecki, 1997) and Mn (Choi, 1998).

---

<sup>5</sup> In principle, modifications to the support as discussed in Section 2.3, should also be considered as promoters. In literature, modifying the support is also termed 'doping'.

## 5. NOVEL APPLICATIONS OF METHANE REFORMING

### 5.1 Sorption-Enhanced Reforming

During a sorption-enhanced reaction process (SERP), one of the reaction products of a catalytic gas phase reaction is separated from the reaction zone by sorption. As a consequence of Le Chatelier's principle<sup>6</sup>, the equilibrium of the reaction is shifted to the product side and conversion of the reactants is increased.

Air Products and Chemicals, Inc. (AP) was the first to investigate the application of SERP to the steam-methane reforming (i.e., sorption-enhanced reforming), reactions (1–3), for the production of H<sub>2</sub> (Hufton, 2000). During this process, CO<sub>2</sub> is extracted from the reaction zone by adsorption onto K-promoted hydrotalcites<sup>7</sup>. As a result, rather large methane conversions can be achieved at relatively mild conditions (i.e., low temperature). In addition, due to the separation of the reaction products CO<sub>2</sub> and H<sub>2</sub>, this process allows for a CO<sub>2</sub>-free production of energy (H<sub>2</sub>).

Initially, AP applied Ni catalysts in their SER process. Their experiments showed that the nickel catalyst removed significant quantities of CO<sub>2</sub> from the reaction gas in addition to the CO<sub>2</sub>-adsorbent. They found that hydrogen was required to remove this 'CO<sub>2</sub>' as CH<sub>4</sub>. Although the form of CO<sub>2</sub> on the catalyst was not determined, this result suggests that ordinary carbon formation rather than adsorption of CO<sub>2</sub> is responsible for the 'CO<sub>2</sub>-consumption' of the Ni catalyst during the SERP. When using noble metal-based catalysts, this particular problem could be avoided.

An additional challenge for reforming at low temperature is the requirement of a catalyst which exhibits high activity at low temperatures.

### 5.2 Hydrogen Membrane Reactors

A similar application of Le Chatelier's principle as for SERP, is the production of hydrogen in membrane reactors (MRs). H<sub>2</sub>-permeable membranes (often Pd or Ag/Pd-based) allow the produced H<sub>2</sub> to permeate through the membrane, parallel to the reaction. Apart from the advantage of producing separate H<sub>2</sub> and CO<sub>2</sub>-flows, the removal of hydrogen from the reaction zone also shifts the equilibrium of the reforming reaction to the product side, just as for SERP. This again makes that high methane conversions can be reached at relatively low temperatures. In addition, Lattner *et al.* (Lattner, 2004) concluded that in, principle, a separate WGS reactor is no longer required, since the removal of H<sub>2</sub> through the membrane leads to sufficiently high CH<sub>4</sub> and CO conversions.

---

<sup>6</sup> "any inhomogeneity that somehow develops in a system should induce a process that tends to eradicate the inhomogeneity."

<sup>7</sup> Hydrotalcite (HTC)-like compounds are layered double hydroxides: MOH-layers separated by anionic interlayers of general formula  $[M^{2+}_{1-x} M^{3+}_x (OH)_2]^+ (A^n)_{x/n} \cdot mH_2O$ . Usually  $M^{2+}$ =Mg and  $M^{3+}$ =Al, but (part of) these metals may be replaced by catalytically active metals such as Ni or Rh. Upon heating (calcination), HTCs undergo a phase transition, in which subsequently H<sub>2</sub>O and – in the case of  $A=CO_3^{2-}$  anions – CO<sub>2</sub> is released, resulting in a mixed metal-oxide. However, due to a "memory effect" of a calcined HTC, the layered structure of metal hydroxides is recreated upon exposure of the mixed oxide to an aqueous solution.

### 5.2.1 Catalytic Aspects of Membrane Reactors

In order to understand the possible problems relating to the catalyst in a SMR-membrane reactor, we should first realize the principle differences between SMR in a conventional reactor and SMR in a membrane reactor. In general, the following differences can be distinguished:

- Mainly due to stability limitations of the membranes, membrane reactors operate at relatively low temperatures, i.e. 400–600°C instead of 800–1000°C. Therefore, performing steam-methane reforming in a MR requires highly active catalysts at low temperatures.
- The steam-reforming reaction under standard conditions is accompanied by a volume expansion of the reaction gas mixture. As a result, an increased pressure negatively affects the CH<sub>4</sub> conversion and decreases H<sub>2</sub> production. In contrast, in a membrane reactor an increased pressure will in principle positively affect the methane conversion, since due to the H<sub>2</sub> removal from the reaction zone, the volume of the reaction gas mixture is reduced during reaction. This has been confirmed by, amongst others, Lin *et al.* (Lin, 2003).
- In a membrane reactor, the H<sub>2</sub> concentration in the reaction gas mixture is low compared to a conventional SR reactor. Consequently, an increased steam-to-carbon ratio is in principle required to prevent carbon formation (see Table 4.1). However, Lægsgaard Jørgensen *et al.* (Lægsgaard Jørgensen, 1995) concluded that, based on thermodynamic calculations, a steam-to-carbon ratio of 2.5 at 500°C and 6 barg would suffice to prevent carbon formation. During conventional SR, a S/C of around 3 is usually applied. This suggests that – in theory – similar values for S/C as applied for conventional SR can be applied for SR in a MR.

With respect to the latter, according to Kikuchi (Kikuchi, 1996), during steam-reforming of methane in a MR, no significant carbon deposition was observed since the rate of H<sub>2</sub> production was significantly higher than that of H<sub>2</sub> permeation. On the contrary, during CO<sub>2</sub>-reforming in a MR, carbon deposition extensively took place on nickel-based catalysts while noble metal-based catalysts showed far less selectivity for carbon formation. This suggests that carbon deposition on nickel-based catalysts becomes more likely with membranes exhibiting high H<sub>2</sub> permeation rates, even for steam-reforming.

Still, the removal of H<sub>2</sub> through a dense Pd- or Pd/Ag-membrane is slow compared to the catalytic reaction rate. As a result, the gas composition near the membrane equals the gas composition in the catalytic bed. Unfortunately, these conditions enhance the risk of carbon formation (Lægsgaard Jørgensen, 1995): In a catalytic system the risk of carbon formation is normally evaluated by means of the so-called Principle of Equilibrated Gas (Rostrup-Nielsen, 1984), stating that carbon formation is to be expected if the gas shows affinity for carbon formation after the establishment of the reforming and shift equilibria (1–3). The principle is developed in the light of the fact that the reforming and water-gas shift reactions are very fast. This means that the feed gas rapidly reaches equilibrium in the catalyst bed. Consequently, the gas near the membrane surface is in chemical equilibrium and the principle can be extended to be valid for the membrane as well as the catalyst.

### 5.2.2 Kinetic Aspects of Membrane Reactors

Lin and co-workers (Lin, 2003) extensively studied the effects of a membrane on the CH<sub>4</sub> conversion and H<sub>2</sub> production by evaluating their experimental results with a kinetic model. Their simulation and experimental results showed that a conversion higher than 80% could be achieved in a palladium membrane reactor at a reaction temperature of 500°C relative to 850°C in a conventional fixed bed reactor. Besides, the yield of CO (<2%) in the MR was much lower than that in a conventional reactor (>50%), which confirmed the significant depression of CO production in a MR discussed above. They also found that an increased reaction pressure results in a higher methane conversion. Further, it was found that the methane conversion strongly depends on the weight hourly space velocity<sup>8</sup> and the amount of methane per membrane surface

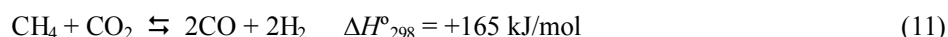
---

<sup>8</sup> WHSV, the hourly weight of inlet methane relative to the loaded catalyst weight (h<sup>-1</sup>).

area (load-to-surface ratio). And finally, the recovery yield of H<sub>2</sub> *decreased* with increasing load-to-surface ratio, whereas the permeation flux of H<sub>2</sub> *increased*. Consequently, a well-balanced value for the load-to-surface ratio should be found.

### 5.3 Reforming of Methane with CO<sub>2</sub>

As an alternative to reforming CH<sub>4</sub> with H<sub>2</sub>O (steam), reforming using CO<sub>2</sub> is also possible. The overall reaction equation for the dry reforming of methane, as it is usually termed, is then:



One of the reasons that dry reforming has received considerable attention is from an environmental point of view, since the greenhouse gas CO<sub>2</sub> is consumed instead of being produced. Also, by adding a certain amount of CO<sub>2</sub> to the feed gas for conventional reforming with steam, it is possible to adjust the H<sub>2</sub>/CO ratio at a range from 1:1 to 3:1 to meet the specific usage.

In principle, catalysts which are active for steam-reforming also work for dry reforming. However, since the steam-to-carbon ratio is lower for dry (or mixed) reforming than for steam reforming, the risk of carbon formation is considerably higher. As a result, research efforts have focussed on catalysts which show high activity to synthesis gas formation, and are also resistant to coking, thus displaying stable long-term operation. In practice, this means that usually the support is the subject of investigation (which we can understand now, after having read Chapter 3 of this report). Especially the rare earth elements (in particular La and Ce) have been identified as suitable candidates for enhancing catalyst performance. See the previous Chapters and, for instance, Ref. (de Pontes, 1997).

## 6. PRESENT TRENDS IN REFORMING-CATALYST RESEARCH

After elaborating on the catalytic aspects of steam reforming, this report will conclude with survey of selected research trends in current SR-catalyst development. It should be noted that, since this field of research is rather vast, this modest survey is not intended to be comprehensive.

Most research in this field is still focussed in improving performance of nickel-based catalysts. More specifically, by modifying the chemical composition of the catalyst support (see Section 3.3) or by promoting the catalyst with 'additives' (see Section 4.2), one aims at achieving longer catalyst life-time (i.e., stability, reducing coke formation) and higher activity (e.g., at lower temperatures). Since these topics are addressed in the previous Chapters, we will focus here on relatively new catalyst research.

More or less in parallel with the line of research addressed above, new types of catalysts are investigated. For instance, carbides such as  $\text{Mo}_2\text{C}$  and  $\text{WC}$  are identified as promising alternatives to current Ni or noble-metal based catalysts (Claridge, 1998). Also  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-x}$  has shown reasonable activity for steam reforming (Ramírez-Cabrera, 2004). In the remainder of this report, however, we will focus on the good old Ni and noble metal catalysts.

### 6.1 Catalyst Preparation using Precursors

An elegant way to obtain active and stable catalysts based on nanoparticles interacting with a metal-oxide matrix is by using precursors, which undergo a phase transition upon heating. Hydrotalcites are often be used for this purpose. For instance, Takehira *et al.* (Takehira, 2004) synthesized a highly dispersed Ni/Mg/Al-oxide catalyst by subsequent calcination and reduction of a hydrotalcite-type precursor containing Ni. Basile *et al.* (Basile, 2004) followed a similar procedure to synthesize Ru and Rh-based noble metal/Mg/Al-oxide catalysts. Tsyganok *et al.* (Tsyganok, 2004) use the 'memory effect'-phenomenon of calcined hydrotalcites to incorporate noble metals into a  $\text{MgAlO}_x$ -matrix, giving highly dispersed and highly active catalysts.

Boehmite ( $\gamma\text{-AlOOH}$ ) impregnated with a metal salt (e.g.,  $\text{RhCl}_3$ ) can be used as a precursor for a highly dispersed  $\gamma\text{-Al}_2\text{O}_3$  supported Rh catalyst [for a similar application see Ref. (Kurungot, 2004), where a sol-gel technique is used].

### 6.2 Alternative Supports

Apart from the  $\text{CeO}_2$ -promotion of 'standard' supports addressed in the previous Chapters, new types of supports are gaining an increased amount of attention. For instance, naturally occurring pillared clays have been tested as supports. Hao *et al.* (Hao, 2003) investigated Zr-Laponite pillared clay-based catalysts for  $\text{CO}_2\text{-CH}_4$  reforming and showed good activity and stability. In the same research group, similar results are obtained by Wang *et al.* for Ni/La-pillared clays catalysts (Wang, 1998e).

More recently, the use of molecular sieves and zeolites as precursors or supports have come into fashion. Zeolites exhibit a well-defined structure and the properties of the active metal can therefore be accurately controlled. For instance, Luo and co-workers investigated the performance of Ni- $\text{La}_2\text{O}_3$  on 5A molecular sieve for the  $\text{CH}_4$  reforming with  $\text{CO}_2$  (Luo, 1999).

Even more interestingly, is the research of Hashimoto *et al.* (Hashimoto, 2002), who synthesized a Ru–CeO<sub>2</sub>/MZ catalyst for CH<sub>4</sub>-CO<sub>2</sub> reforming at low temperatures (MZ = mordenite zeolite). The catalyst with MZ as a support resulted in highly dispersed Ru and CeO<sub>2</sub>. This catalyst shows high activity and low carbon deposits – hence, a promising class of low-temperature reforming catalysts!



## REFERENCES

- Anderson, J.R. and K.C. Pratt (1985): *Introduction to characterization and testing of catalysts*, Academic Press.
- Ayabe, S., H. Omoto, T. Utaka, R. Kikuchi, K. Sasaki, Y. Teraoka and K. Eguchi (2003): *Catalytic autothermal reforming of methane and propane over supported metal catalysts*; *Applied Catalysis A* 241: 261-269.
- Basile, F., G. Fornasari, V. Rosetti, F. Trifirò and A. Vaccari (2004): *Effect of the Mg/Al ratio of the hydrotalcite-precursor on the dispersion and activity of Rh and Ru catalysts for the partial oxidation of methane*; *Catalysis Today* 91-92: 293-297.
- Bengard, H.S., J.K. Nørskov, J.S. Sehested, B.S. Clausen, L.P. Nielsen, A.M. Molenbroek and J.R. Rostrup-Nielsen (2002): *Journal of Catalysis* 209: 365.
- Bodrov, N.M., L.O. Apel'baum and M.I. Temkin (1964): *Kinetics of the reaction of methane with water vapor on a nickel surface*; *Kinetics and Catalysis* 5: 614.
- Bodrov, N.M., L.O. Apel'baum and M.I. Temkin (1967): *Kinetics and Catalysis* 8: 696.
- Borowiecki, T., A. Gołębiowski and B. Stasińska (1997): *Effects of small MoO<sub>3</sub> additions on the properties of nickel catalysts for the steam reforming of hydrocarbons*; *Applied Catalysis A* 153: 141-156.
- Bradford, M.C.J. and M.A. Vannice (1996): *Catalytic reforming of methane with carbon dioxide over nickel catalysts. I. Catalyst characterization and activity*; *Applied Catalysis A* 142: 73-96.
- Choi, J.S., K.I. Moon, Y.G. Kim, J.S. Lee, C.H. Kim and D.L. Trimm (1998): *Stable carbon dioxide reforming of methane over modified Ni/Al<sub>2</sub>O<sub>3</sub> catalysts*; *Catalysis Letters* 52: 43-47.
- Claridge, J.B., A.P.E. York, A.J. Brungs, C. Marquez-Alvarez, J. Sloan, S.C. Tsang and M.L.H. Green (1998): *New catalysts for the conversion of methane to synthesis gas: Molybdenum and tungsten carbide*; *Journal of Catalysis* 180: 85-100.
- Craciun, R., W. Daniell and H. Knözinger (2002): *The effect of CeO<sub>2</sub> structure on the activity of supported Pd catalysts used for methane steam reforming*; *Applied Catalysis A* 230: 153-168.
- Dong, W.S., H.S. Roh, K.W. Jun, S.E. Park and Y.S. Oh (2002): *Methane reforming over Ni/Ce-ZrO<sub>2</sub> catalysts: effect of nickel content*; *Applied Catalysis A* 226: 63-72.
- Frennet, A., G. Lienard, A. Crucq and L. Degols (1978): *Journal of Catalysis* 53: 150.
- Hao, Z., H.Y. Zhu and G.Q. Lu (2003): *Zr-Laponite pillared clay-based nickel catalysts for methane reforming with carbon dioxide*; *Applied Catalysis A* 242: 275-286.
- Hashimoto, K., S. Watase and N. Toukai (2002): *Reforming of methane with carbon dioxide over a catalyst consisting of ruthenium metal and cerium oxide supported on mordenite*; *Catalysis Letters* 80: 147-152.
- Hou, Z. and T. Yashima (2003): *Small amounts of Rh-promoted Ni catalysts form methane reforming with CO<sub>2</sub>*; *Catalysis Letters* 89: 193-197.
- Hufton, J.R., S.J. Weigel, W.F. Waldron, M. Rao, S. Nataraj, S. Sircar and T.R. Gaffney (2000): *Sorption enhanced reaction process for production of hydrogen; DOE-Air Products Cooperative Agreement*; Instrument #DE-FC36-95G010059 .
- Kikuchi, E. (1996): *Steam reforming and related reactions in hydrogen-permselective*

- membrane reactor*; Sekiyu Gakkaishi 39: 301-313.
- Kurungot, S. and T. Yamaguchi (2004): *Stability improvement of Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst layer by ceria doping for steam reforming in an integrated catalytic membrane reactor*; Catalysis Letters 92: 181-187.
- Lattner, J.R. and M.P. Harold (2004): *Comparison of conventional and membrane reactor fuel processors for hydrocarbon-based PEM fuel cell systems*; International Journal of Hydrogen Energy 29: 393-417.
- Lægsgaard Jørgensen, S., P.E. Højlund Nielsen and P. Lehrmann (1995): *Steam reforming of methane in a membrane reactor*; Catalysis Today 25: 303-307.
- Lin, Y.M., S.L. Liu, C.H. Chuang and Y.T. Chu (2003): *Effect of incipient removal of hydrogen through palladium membrane on the conversion of methane steam reforming: Experimental and modeling*; Catalysis Today 82: 127-139.
- Luo, J.Z., L.Z. Gao, C.F. Ng and C.T. Au (1999): *Mechanistic studies of CO<sub>2</sub>/CH<sub>4</sub> reforming over Ni-La<sub>2</sub>O<sub>3</sub>/5A*; Catalysis Letters 62: 153-158.
- Masel, R.I. (1996): *Principles of adsorption and reaction on solid surfaces*, Wiley-Interscience, New York.
- Masel, R.I. (2001): *Chemical kinetics and catalysis*, Wiley-Interscience, Chichester.
- Matsumura, Y. and T. Nakamori (2004): *Steam reforming of methane over nickel catalysts at low reaction temperature*; Applied Catalysis A 258: 107-114.
- Nielsen, B., A.C. Luntz, P.M. Holmblad and I. Chorkendorff (1995): Catalysis Letters 32: 15.
- Noronha, F.B., A. Shamsi, C. Taylor, E.C. Fendly, S. Stagg-Williams and D.E. Resasco (2003): *Catalytic performance of Pt/ZrO<sub>2</sub> and Pt/Ce-ZrO<sub>2</sub> catalysts on CO<sub>2</sub> reforming of CH<sub>4</sub> coupled with steam reforming or under high pressure*; Catalysis Letters 90: 13-21.
- Pontes, M. de, R.L. Espinoza, C.P. Nicolaides, J.H. Scholtz and M.S. Scurrall (1997): *Natural Gas Conversions IV*; Studies in Surface Science and Catalysis, 491-560.
- Ramírez-Cabrera, E., A. Atkinson and D. Chadwick (2004): *Catalytic steam reforming of methane over Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2-x</sub>*; Applied Catalysis B 47: 127-131.
- Roh, H.S., H.S. Potdar, K.W. Jun, J.W. Kim and Y.S. Oh (2004): *Carbon dioxide reforming of methane over Ni incorporated into Ce-ZrO<sub>2</sub> catalysts*; Applied Catalysis A 276: 231-239.
- Rostrup-Nielsen, J.R. (1984): *Catalytic Steam Reforming*; Editors: J.R. Anderson and M. Boudart, *Catalysis: Science and Technology*, Springer.
- Rostrup-Nielsen, J.R. and J.-H. Bak Hansen (1993): *CO<sub>2</sub>-reforming of methane over transition metals*; Journal of Catalysis 144: 38-49.
- Rostrup-Nielsen, J.R., J. Sehested and J.K. Nørskov (2002): *Hydrogen and synthesis gas by steam- and CO<sub>2</sub> reforming*; Advances in Catalysis 47: 65-139.
- Sehested, J., A. Carlson, T.V.W. Janssens, P.L. Hansen and A.K. Datye (2001): Journal of Catalysis 197: 200.
- Smith, D.J. and L.D. Marks (1981): Philosophical Magazine A 44: 735.
- Somorjai, G.A. (1972): *On the mechanism of sulfur poisoning of platinum catalysts*; Journal of Catalysis 27: 453.
- Somorjai, G.A. (1994): *Introduction to surface chemistry and catalysis*, Wiley Interscience, New York.
- Swartz, S.L. (2003): *Nano-scale water-gas-shift catalysts*; DOE CARAT Program.

- Takatani, S. and Y.W. Chung (1984): *Strong metal-support interaction in Ni/TiO<sub>2</sub>: Auger and vibrational spectroscopy evidence for the segregation of TiO<sub>x</sub> (x~1) on Ni and its effects on CO chemisorption*; Journal of Catalysis 90: 75-83.
- Takehira, K., T. Shishido, P. Wang, T. Kosaka and K. Takaki (2004): *Autothermal reforming of CH<sub>4</sub> over supported Ni catalysts prepared from Mg-Al hydrotalcite-like anionic clay*; Journal of Catalysis 221: 43-54.
- Thomas, J.M. and W.J. Thomas (1967): *Introduction to the principles of heterogeneous catalysis*, Academic Press, London.
- Tsyganok, A.I., M. Inaba, T. Tsunoda, K. Suzuki, K. Takehira and T. Hayakawa (2004): *Combined partial oxidation and dry reforming of methane to synthesis gas over noble metals supported on Mg-Al mixed oxide*; Applied Catalysis A 275: 149-155.
- Twigg, M.V. (1989): *Catalyst Handbook*, Wolfe Publishing Ltd.
- Udengaard, N.R., J.-H.B. Hansen and D.C. Hanson (1992): Oil & Gas Journal 90: 62.
- Verykios, X.E. (2003): *Catalytic dry reforming of natural gas for the production of chemicals and hydrogen*; International Journal of Hydrogen Energy 28: 1045-1063.
- Wang, S. and G.Q. Lu (1996): *Carbon dioxide reforming of methane to produce synthesis gas over metal-supported catalysts: State of the art*; Energy & Fuels 10: 896-904.
- Wang, S. and G.Q. Lu (1998a): *Catalytic activities and coking characteristics of oxides-supported Ni catalysts for CH<sub>4</sub> reforming with carbon dioxide*; Energy & Fuels 12: 248-256.
- Wang, S. and G.Q. Lu (1998b): *CO<sub>2</sub> reforming of methane on Ni catalysts: Effect of the support phase and preparation technique*; Applied Catalysis B 16: 269-277.
- Wang, S. and G.Q. Lu (1998c): *Reforming of methane with carbon dioxide over Ni/Al<sub>2</sub>O<sub>3</sub> catalysts: Effect of nickel precursor*; Applied Catalysis A 169: 271-280.
- Wang, S. and G.Q. Lu (1998d): *Role of CeO<sub>2</sub> in Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts for carbon dioxide reforming of methane*; Applied Catalysis B 19: 267-277.
- Wang, S., H.Y. Zhu and G.Q. Lu (1998e): *Preparation, characterization, and catalytic properties of clay-based nickel catalysts for methane reforming*; Journal of Colloid and Interface Science 204: 128-134.
- Wei, J. and E. Iglesia (2004): *Structural requirements and reaction pathways in methane activation and chemical conversion catalyzed by rhodium*; Journal of Catalysis 225: 116-127.
- Xu, and G.F. Froment (1989): *Methane steam reforming, methanation and water-gas shift: I. Intrinsic kinetics*; AIChE Journal 35 (1): 88-96.
- Yamazaki, O., T. Nozaki, K. Omata and K. Fujimoto (1992): Chemistry Letters : 1953-1954.
- Yokota, S., K. Okumura and M. Niwa (2002): *Support effect of metal oxide on Rh catalysts in the CH<sub>4</sub>-CO<sub>2</sub> reforming reaction*; Catalysis Letters 84: 131-134.
- Zhang, Z. and X.E. Verykios (1996): *Carbon dioxide reforming of methane to synthesis gas over Ni/La<sub>2</sub>O<sub>3</sub> catalysts*; Applied Catalysis A 138: 109-133.