Chapter 6
Syngas Production Using Carbon Dioxide Reforming: Fundamentals and Perspectives

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6.1 Introduction

Much has been written over the last few decades about the potential use of CO_2 as a feedstock in the chemical industry, and particular attention has been given to its possible use in the conversion of methane and other hydrocarbons using so-called dry reforming to give syngas, a mixture of CO and hydrogen. The CO_2 or dry reforming of methane can be represented by the equation

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \tag{6.1}$$

In any practical application, in order to achieve acceptable conversions, this reaction would have to be carried out at very high temperature (up to as much as 1,000 °C) when the conversion would be close to chemical equilibrium. The reaction is always accompanied by the reverse water–gas shift reaction, generally fully at equilibrium:

$$CO_2 + H_2 \rightleftarrows CO + H_2O \tag{6.2}$$

A consequence of the combination of these two reactions is that the $CO:H_2$ ratio obtained is generally rather lower than the value of 1:1 to be expected if only the reaction of Eq. 6.1 occurred. The reaction system is further complicated by the fact that the conditions used generally favour carbon deposition. Carbon deposition can be thought of as occurring by one of three interdependent reactions:

$$2CO \rightleftarrows C + CO_2 \tag{6.3}$$

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$$CH_4 \rightleftarrows C + 2H_2 \quad (6.4)$$

and

$$CO + H_2 \rightleftarrows C + H_2O \quad (6.5)$$

In most practical cases, whether or not carbon deposition is likely to occur is determined by thermodynamic considerations; further, as Boudouard carbon (Eq. 6.3) is generally expected at low temperatures, carbon deposition under dry reforming conditions is most likely to occur by either methane decomposition (Eq. 6.4) or CO reduction (Eq. 6.5). The problem of carbon deposition is a key feature of the process and we will return to it many times below.

A search of Web of Science using the search terms "methane, CO_2 and reforming" shows that more than 1,900 papers with these three words in the titles and/or abstracts had been published between 1987 and mid-2013. Table 6.1 shows the approximate number of papers that include these search terms published up to 1994 and in each 5-year period since then, together with the approximate total number of citations to these papers given in each period. It is clear that there is little sign of the interest in the subject showing any decline; indeed, the yearly number of publications reached an all-time high of more than 200 in 2012, this being significantly higher than the previous maximum of 160 in 2011. As will be discussed further below, it is highly questionable if this level of activity is justified by the potential applicability of the process. The only justification for such a level of activity is probably that the work reported provides new insights into particular types of catalysts, CO_2 reforming being used as a model reaction.

Other combinations of search terms to those used in the search of the Web of Science discussed above show up significant additional material.[1] This review is based largely on the material gleaned from the search related to Table 6.1. However, some references are also included that did not show up in this search, in most cases because the keywords of the original articles were different; there is also no doubt that some important papers will have been omitted for the same reason.

Interestingly, the first paper on CO_2 reforming of methane listed in the search outlined in Table 6.1 is a relatively under-cited one by Fish and Hawn on the use of CO_2 reforming in a thermochemical cycle [1], a topic to which we will return briefly below. The second paper on the list, by Gadalla and Bowers [2], is concerned with the use of a range of commercial steam reforming catalysts, showing that the most promising results were obtained with alumina supports containing magnesium or calcium oxide. (A further paper by Gadalla and Somer [3], published in 1989, gives more details on this subject.) As will be discussed in a later section, Ni catalysts based on Mg-containing supports still appear to be among the most effective catalysts for the process.

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[1] No attempt has been made to cross-check the contents of various searches that have been carried out so that the total number of papers is likely to be well in excess of 2000. More detailed Web of Science and Scopus searches have also been carried out in order to identify some of the key references on each of these subjects, and the text that follows below concentrates predominantly on these papers.

Table 6.1 The numbers of papers on the topic of dry reforming of methane published during various time periods since 1987 together with the numbers of citations listed in those time periods

Years	Up to 1995	1996–2000	2001–2005	2005–2010	2011 and later
Publications	60	280	490	670	>400
Citations	<200	2,400	7,200	1,890	1,380

Data obtained from a Web of Science (Thomson Reuters) search (May 2013) using the search terms *methane, CO_2 and reforming*

Many of the papers that have been published over the last 20 years or so justify the work carried out by claiming that a process involving the consumption of both methane and CO_2 would help to provide a solution to the emission of these two greenhouse gases. It needs to be emphasised from the outset that such claims are largely unjustified since the quantity of CO_2 that might be used in syngas production by CO_2 reforming would be negligible compared with the very large emissions of CO_2 currently causing concern, even if it was possible to collect the CO_2 in a sufficiently pure form for the CO_2 reforming reaction. Further, dry reforming produces syngas with a composition usable only in limited applications; as shown above (see Eq. 6.1), using methane as co-reactant, the syngas ratio, CO/H_2, is approximately 1.0. Much more suitable ratios can be attained by the addition of either steam or oxygen to the reactant stream, such addition also having the benefit that the potential for carbon deposition on the catalysts used in the process is significantly reduced.[2] An alternative to the dry reforming process using CO_2 in the primary feed is to operate the steam reforming reaction:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{6.6}$$

and then to carry out the reverse water–gas shift reaction (reverse of reaction (6.2)) in order to achieve the desired CO/H_2 ratio:

$$CO_2 + H_2 \rightarrow CO + H_2O \tag{6.7}$$

There are several advantages to be achieved using this approach, these including the following: (i) the problem of C deposition can largely be avoided since the catalysts and process conditions for the steam reforming reaction under carbon-free conditions are well established commercially; and (ii) the CO_2 required for the process can be extracted from the effluent of the reformer furnace (burning natural gas) used to heat the tubular steam reforming reactor system. Hence, the only additional processing step required is the separation unit to remove CO_2 from the combustion gases, a step also required if dry reforming is to be carried out. Further, although the cost of a steam reforming plant is very high and a major contributor to the all-over cost of any process requiring a syngas feed, it is unlikely that there will be much reduction in the total operation cost if dry reforming is used.

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[2] A relatively small proportion of the papers in the recent literature have recognised these further limitations, and some of these are listed in the tables below.

Accepting, for the reasons given above, that dry reforming is unlikely to solve the greenhouse gas problem, other justifications have to be found for the very extensive work on the subject that has been carried out over recent years. As will be discussed in more detail in the following sections, much of the most recent work has been devoted to trying to find catalysts that are resistant to carbon deposition while having suitable activities and stabilities under reaction conditions.[3] Although much of the work published recently undoubtedly adds incrementally to the literature of the subject, there appear to have been no major breakthroughs: most, if not all, of the catalysts that have been examined under suitable conditions unfortunately show gradual deactivation due to carbon deposition. Further, many of the catalyst systems studied bear remarkable similarity to ones that have been studied previously for other closely related reactions, for example, the steam reforming of methane. In many cases, such similarities do not appear to have been recognised by the authors of these papers.

This review traces briefly the development of processes used for the production of syngas from methane (and higher hydrocarbons) and discusses the interest in the use of CO_2 as a co-reactant, paying particular attention to the conversion of methane. It then considers the thermodynamics of such conversion processes, highlighting the problem of carbon deposition and the need for operation at high temperature. Recognising the similarity between dry reforming and steam reforming and the fact that the latter is a well-established industrial process, mention is made of the catalysts used commercially for the steam reforming of methane and of higher hydrocarbons, with a short digression on the catalysts used for methanation. The review then considers various groups of papers that have been devoted to studies of different catalyst types, particular attention being given to the use of noble metals (particularly Pt) and other transition metals such as Ni, Co and Mo, on a variety of different supports. The review concentrates on the literature on methane reforming, but it should be recognised that many of the catalysts developed will be equally applicable to the reforming of higher hydrocarbons, the only complication being that methane is also a potential product when the methanation reaction is thermodynamically feasible (at lower temperatures, see Sect. 6.2.2).

6.2 Historical Background

6.2.1 Syngas Production from Hydrocarbons

Before embarking on a more detailed discussion of the dry reforming reaction and the catalysts that have been used for that reaction, it is sensible first to give a brief

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[3] Unfortunately, a significant proportion of the papers in the recent literature report experiments carried out under unrealistic conditions, for example, at low temperatures or with non-stoichiometric reactant compositions; in any process that will be developed, the reaction will be carried out at high temperatures and pressures under conditions close to equilibrium, and any novel catalyst formulations must be tested under similar conditions.

outline of the use and importance of the steam reforming of methane as a source of syngas. The subject of the steam reforming of methane (Eq. 6.6) has been reviewed by various different authors, from the point of view of both the processes involved [4] and of the catalysts used [5]. Although, as pointed out by Rostrup-Nielsen [4], some papers and patents on the steam reforming of hydrocarbons had been published as early as 1868, the first industrial steam reformer was commissioned in Baton Rouge in 1930 by the Standard Oil of New Jersey, and this was followed by another reformer commissioned by ICI in Billingham in 1936; in both cases, the main product required was hydrogen, and so the CO formed was removed using the water–gas shift reaction. While steam reforming in the United States was usually carried out with methane as the feed hydrocarbon, the raw material of choice in Europe until the 1960s was naphtha; with the advent of European natural gas supplies in the second half of that decade, methane also became the feedstock of choice.[4] It is interesting to note that although there has been some limited commercial interest in the use of CO_2 as a feed instead of water, the only plant using a methane/CO_2 feedstock has been a pilot plant operated by Haldor Topsoe in Texas in which a sulphur-modified steam reforming catalyst is used [6]. It is also worth noting that in the so-called Midrex process for the direct reduction of iron ore, a mixed feed of methane with CO_2 and steam is used in a reformer; the CO_2 and steam for the reforming step are produced during the reduction of the iron ore, and the syngas produced in the reformer is fed directly to the reduction reactor [6, 7].

Although other active materials, notably the noble metals, have been examined for use as the active components in steam reforming catalysts, the only ones that have been used commercially are those including Ni as the active component. This is not only a matter of cost: Ni is the only non-noble transition metal that is maintained in its metallic state under steam reforming conditions since the equilibrium

$$NiO + H_2 \rightleftarrows Ni + H_2O \tag{6.8}$$

lies to the right-hand side as long as the ratio H_2/H_2O is greater than about 0.01; in other words, the nickel will be in its reduced (and active) form as long as there is approximately 1 % hydrogen in the reactant gas [5]. (With the exception of the noble metals, much higher proportions are needed for most of the other transition metals.) A variety of different Ni-containing formulations have been commercialised. However, among the most commonly used materials are the ICI (now Johnson Matthey) 46–1 catalyst (predominant components in the reduced form are Ni, alumina and K_2O with CaO, SiO_2 and MgO added as a cement binder) and the Haldor Topsoe catalyst (containing Ni, MgO and alumina). Other catalyst manufacturers supply similar materials. The potassium of the ICI formulation is added to help minimise C deposition, and the MgO of the Haldor Topsoe material

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[4] Syngas could also be formed by coal gasification or by modifications of the gasification process using steam or CO_2 in the feed.

serves a similar function. As mentioned above, the catalyst used in the Haldor Topsoe pilot plant for dry reforming (see above) is partially sulphided [4, 6, 8]. This was based on work on the subject of S passivation for application in the steam reforming process [9].

6.2.2 Methanation

From a historical point of view but also in relation to work on the formulation of catalysts, it is interesting to note that there occurred in the late 1970s and early 1980s a period of very significant academic and industrial research activity on the topics of methanation and methanation catalysts. This interest arose because natural gas supplies in the United States could not keep up with demand. As a result, it was desirable to find means of converting syngas (produced from coal) into so-called synthetic natural gas (SNG):

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{6.9}$$

This reaction is the reverse of the steam reforming reaction (Eq. 6.6) and is highly exothermic. Hence, much of the work from that period concentrated on finding catalysts with high stability at higher temperatures that also resisted carbon deposition. Many of the catalysts examined and reported in many papers of that period had great similarity to those that have been examined more recently for dry reforming. This author reviewed the literature on methanation and steam reforming in 1985 [10].

6.2.3 Methane Coupling

Following on from the great interest from the catalysis community in the topic of methanation, the subject of the oxidative coupling of methane to give C_2H_6 and C_2H_4 became predominant during the second half of the 1980s as a result of a paper by Keller and Bhasin published in 1982 [11]. These authors showed that it was possible, using a cyclic process in which methane and oxygen were fed in turn to a catalyst bed, to obtain reasonable yields of C_2 hydrocarbons, the catalysts being operated at temperatures around 800 °C. Keller and Bhasin used a range of α-alumina-supported materials (including the oxides of Cd, Sn, Sb, Tl, Bi and Pb) as catalyst and postulated that an oxidation–reduction mechanism was involved. Hinsen and Baerns were the first to carry out the reaction with methane and oxygen fed simultaneously, and they obtained good yields using a lead/γ-alumina catalyst [12]. A paper by Ito, Wang, Lin and Lunsford published in 1985 introduced the use of Li/MgO materials [13]. Many more similar catalysts were introduced over the next decade, and a number of very extensive reviews have been written on the subject [14–17].

It was soon recognised that the reaction occurs by a combination of heterogeneous reactions and gas-phase radical reactions and that the products included not only ethane and ethylene but also a mixture of higher hydrocarbons, water, CO, CO_2 and hydrogen. The participation of gas-phase reactions as well as limitations introduced by the explosive limits of methane/oxygen mixtures leads to a limit in the potential yields of C_2 hydrocarbons produced in the reaction, the best values being just above 20 %, too low to enable the reaction to have commercial application with current natural gas prices. Although papers on the subject were published in a variety of different journals, a very good overview of the work that was carried out is to be found by examining the proceedings of the earlier "Natural Gas Conversion" meetings [18–21], from the first of the series held in 1987 in Auckland, NZ, to the fourth meeting held in 1998 in Messina, Italy; by 2001, when the 6th meeting of the series was held in Alaska, the topic of methane coupling had disappeared. What had been gained from all this work was a much greater understanding in the academic community of the operation of catalytic reactors at elevated temperatures and the problems of catalyst stability. (It is of interest to note that renewed interest in methane coupling has recently been evident, this being spurred by the current low prices of natural gas.)

6.2.4 Dry Reforming and Partial Oxidation of Methane

When at the beginning of the 1990s an interest developed in the production of syngas from natural gas using either partial oxidation or "dry reforming", it was not surprising that the research community that had been involved in the work on methane coupling transferred its interest to studying one or other of these two reactions. This transfer is clearly seen in the proceedings of the "Natural Gas Conversion" meetings referred to above. The majority of the papers under the title "Methane Conversion" in the second meeting held in Oslo in 1990 [18] were related to oxidative coupling, there being none on partial oxidation or CO_2 reforming. This bias was continued at the third meeting held in Sydney in 1993 [19] with more than 20 papers on methane coupling and only four on dry reforming; two of the latter were reviews of the subject by J. R Rostrup-Nielsen and by J. H. Edwards and A. M. Maitra (discussed further in the following section). However, by the time of the fourth meeting held in the Kruger National Park in South Africa in 1995 [20], there were 16 papers on oxidative coupling, 13 papers on partial oxidation and 8 papers on CO_2 reforming. By the fifth meeting held in Taormina, Italy, in 1998 [21], the latter two topics had become the predominant subjects of interest related to methane conversion. The relevant papers from these meetings will be outlined in Sect. 6.4.1.

As discussed above (see Table 6.1), there has since 1996 been an explosive development of interest in CO_2 reforming and partial oxidation, so much so that it is virtually impossible to write a comprehensive review covering every aspect of the work that has been carried out on either topic. The following sections will therefore concentrate on some of the more important types of catalyst that have been investigated, particular attention being paid to papers describing those types of catalyst that have reasonable stabilities under “dry reforming” conditions and to papers giving new insights into the mechanism of the reaction or advancing other approaches to the conversion process. No great detail on any of the papers is given; instead, summaries are given in tabular form of their main conclusions. Further, no attempt is made to discuss any of the parallel literature on partial oxidation, exceptions being when it has been shown that the addition of oxygen to the “dry reforming” mixture has beneficial effects or when the results on the partial oxidation reaction on a particular catalyst have some relevance to the dry reforming reaction on identical or similar catalysts. In selecting the literature for inclusion, use has been made of citation indexing, the searches being based on the use of Web of Science and/or Scopus. As a starting point, some of the papers appearing in the proceedings of the earlier Natural Gas Conversion meetings referred to above have been used to identify some of the major themes of research. Scopus and Web of Science searches have then been used to identify some of the (in most cases) more recent key papers related to each of these themes, and some of the main conclusions of these are tabulated. Finally, the main objectives and conclusions of some very recently published papers on the subject that have not yet achieved a significant citation record are summarised.

Before embarking on our summary of the literature, a brief outline of the thermodynamic limitations associated with the dry reforming reaction and associated side reactions is given since these limitations have some importance in discussing the papers from the literature.

6.3 Thermodynamics of the CH_4 + CO_2 Reaction

The dry reforming of methane (Eq. 6.1) is an endothermic process, and so the maximum conversion calculated thermodynamically increases with increasing temperature. This is illustrated schematically in Fig. 6.1 that shows the thermodynamic conversions for various feed compositions as a function of temperature of reaction [22]. It can be seen that a temperature in excess of about 850 °C is necessary to obtain adequate conversions using a stoichiometric CH_4/CO_2 feed (1:1).

It is to be expected that the water–gas shift reaction (Eq. 6.2) will be in equilibrium under CO_2 reforming conditions and so the CO/H_2 ratio of the product gas can be calculated easily from a knowledge of the feed compositions and the measured methane conversions. It should be noted that the so-called selectivity of the reaction is very frequently given in publications reporting the behaviour of novel catalysts; unless it is shown very clearly that the water–gas reaction is *not* in equilibrium for that catalyst system, such values have no real significance as they are thermodynamically rather than kinetically controlled.

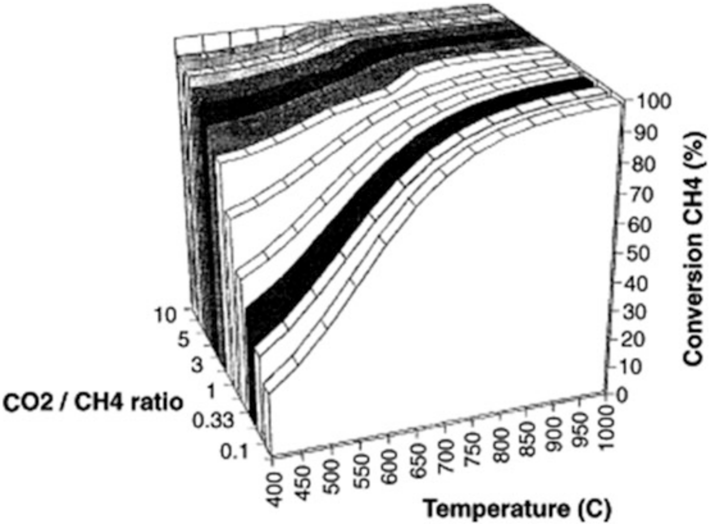

Fig. 6.1 Thermodynamically calculated conversions of methane as a function of temperature for a series of different feed ratios. Calculations carried out using HSC chemistry (version 1.10, Outokumpu Research, Finland) (Reprinted from Ref. [22]. Copyright 2005, with permission from Elsevier)

Figure 6.2 shows the yield of carbon to be expected if carbon deposition is possible for two possible cases: whether or not the water–gas shift reaction is considered to be in equilibrium [22]. This diagram was constructed assuming that there is a closed system and that the amount of carbon formed relates to the amount fed as methane and CO_2; the results should therefore be seen only as a guide as to when carbon would form in a continuous flow reactor. It is clear that carbon formation is possible over the whole range of temperatures in both cases considered (with or without the water–gas shift reaction being equilibrated), and that the amount of carbon formed will be lower at high temperatures. When the water–gas shift reaction does not take place, the amount formed at the highest temperatures is much lower; however, in most cases reported in the literature, the water–gas shift reaction is at equilibrium at the higher temperatures and so this situation does not apply. Rostrup-Nielsen uses a different approach, favouring the use of so-called carbon limit diagram, developed first for the steam reforming reaction [6, 23]. He shows that in the absence of the addition of steam, the CO_2 reforming reaction operates under conditions when carbon can form regardless of the CH_4/CO_2 ratio. He concludes that the noble metals, most of which do not form carbides (necessary intermediates in carbon formation) have a greater potential for use as CO_2 reforming than do catalyst formulations using nickel. The topic of carbon deposition will be handled further after a discussion of the types of catalyst studied.

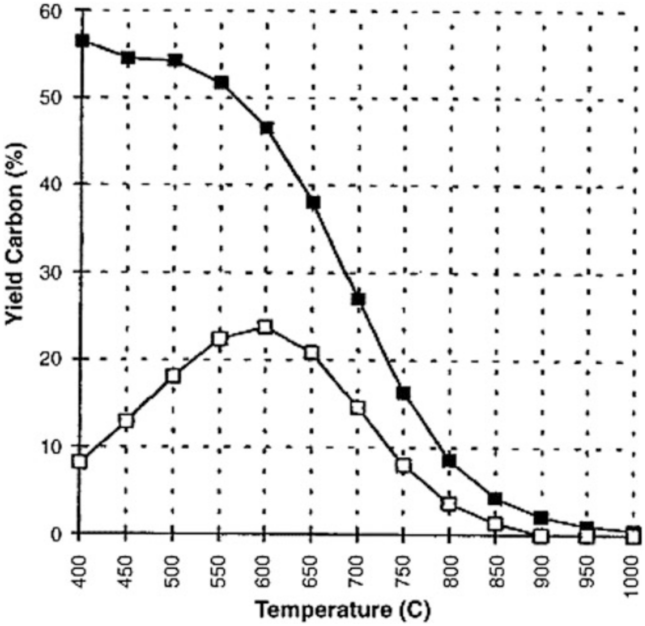

Fig. 6.2 Thermodynamically calculated proportions of carbon formed under CO_2 reforming conditions with $CH_4/H_2O = 1.0$; (■), with the reverse water–gas shift reaction in equilibrium; (□), without the reverse water–gas shift reaction (Reprinted from Ref. [22]. Copyright 2005, with permission from Elsevier)

6.4 Catalysts for the Dry Reforming of Methane

6.4.1 Papers on CO_2 Reforming Published in the Proceedings of the Natural Gas Conversion Symposia up to 1998

Tables 6.2, 6.3, and 6.4 list the relevant papers presented at the Natural Gas Conversion Symposia between 1993 and 1998: the third (held in 1993, published in 1994 [19]), the fourth (held in 1995, published in 1997 [20]) and the fifth (held and published in 1998 [21]). The following paragraphs first summarise two review articles from the third meeting and then outline some of the important aspects of the other papers, this being in preparation for a more general discussion of the literature on the subject since about 1997.

In his review delivered at the third symposium [6], Rostrup-Nielsen of Haldor Topsoe A/S (Lyngby, Denmark) gave a very clear exposition of the then-available information on the CO_2 reforming of methane, paying particular attention to earlier work on the subject. He noted that the reaction was examined by Fischer and

Table 6.2 Papers from NGC 3

Reference/year	Metal	Support	Temperature range/°C	Comments
Rostrup-Nielsen [6]	Noble metals S-passivated nickel	Alumina MgO	No specific range given	Review article, discussing process options and carbon deposition; also summarises some work from Haldor Topsoe on noble metals as CO_2 reforming catalysts
Edwards [24]	Range	Range	No specific range given	Review article, summarising types of catalysts studied up to about 1993; some discussion of possible processes
Seshan [25]	Pt, Ni	ZrO_2, Al_2O_3	390–560	Pt/ZrO_2 much more stable that Pt/Al_2O_3; 5%Ni/ZrO_2 more stable than 10%Ni/ZrO_2
Uchijima [26]	Rh	Al_2O_3, SiO_2, TiO_2	377–727	PO gives first combustion and then steam and CO_2 reforming. Rh/Al_2O_3 is 35× more active than Rh/SiO_2 for CO_2 reforming. Addition of Al_2O_3 or TiO_2 to Rh/SiO_2 gives significant promotion

Tropsch as early as 1928 [49]; these scientists studied a series of base metal catalysts and found that nickel and cobalt gave the best results, the product gas compositions being close to thermodynamic equilibrium.

Rostrup-Nielsen also summarises the work of Bodrov and Apel'baum who showed in 1967 [50] that the kinetic expression for the CO_2 reforming reaction over a nickel film was similar to what they had found previously for the steam reforming reaction [51], this indicating that the mechanism was very similar for both reactions.

Rostrup-Nielsen discussed industrial processes that involve CO_2 reforming, these including the SPARG process making use of a sulphur-passivated Ni catalyst. The original research relating to that process is detailed in a research paper by Dibbern et al. referred to above [8]. The technology used, adding traces of H_2S to the reactor feed, is similar to that previously introduced by Haldor Topsoe to enable steam reforming to be carried out at low steam/methane ratios [9]. Rostrup-Nielsen also presented in his review some data on the CO_2 reforming of methane using the noble metals and Ni supported on MgO. He concluded that the noble metals are much less susceptible to carbon poisoning due to the fact that they do not dissolve C in their bulk. He then described briefly some work in which Rh and Ru catalysts, the

Table 6.3 Papers from NGC4

Reference/ year	Metal	Support	Temperature range/°C	Comments
Cant [27]	Ni, Rh	Al_2O_3	700	Deuterium kinetic isotope effect shows differences between metals. C easily removed from Rh
Slagtern [28]	Ni	Al_2O_3	700, 800	Rare earth mixture used as promoter; similar results to using La_2O_3
Yu [29]	Ni	Al_2O_3	700, 750	CH_4 decomposition, followed by removal of C by CO_2
Zhang [30]	Ni	La_2O_3	550–750	L_2O_3 activates CO_2 and encourages removal of C from Ni
Erdöhelyi [31]	Ir	Al_2O_3, TiO_2, SiO_2, MgO	427–500, 850	C deposition limited on all samples. TiO_2 most effective support
Van Keulen [32]	Pt	ZrO_2	550–800	Optimisation of Pt/ZrO_2 with life tests
Kikuchi [33]	Ni, noble metals	Al_2O_3	500	Tested in membrane reactor system. Noble metals much less susceptible to coke formation
Ponelis [34]	Ru, Rh	SiO_2	400–900	Membrane gives significantly improved conversions at higher contact times

most promising of the metals studied, were used for carbon-free operation in a pilot plant under conditions in which carbon is favoured thermodynamically. He concluded, however, that because of their scarcity neither of these metals is likely to be used in other than niche applications. In conclusion, Rostrup-Nielsen discussed the limitations of possible processes for the use of CO-rich gases from CO_2 reforming. He pointed out that the amounts of CO_2 used in such processes will be virtually insignificant in comparison with the total worldwide emissions of CO_2. For example, the CO_2 that would be required for the production of 5 million tons of acetic acid per year (the current global rate of production) by the reaction:

$$CH_4 + CO_2 \rightarrow CH_3COOH \tag{6.10}$$

would correspond to the emission from only one 500 MW coal-based electricity power station. Yearly worldwide production of methanol is four times higher, and so supplying syngas via CO_2 reforming of methane would require the output from four such power plants. More importantly, the current technology for CO_2 extraction makes the use of CO_2 from flue gases uneconomical and so other sources of CO_2 would have to be considered. The article by Rostrup-Nielsen contains many other details (and warnings) related to the potential of a process for CO_2 reforming. Anyone working in the area should therefore read it with care.

A second review article was delivered at the same symposium; this was reported by Edwards and Maitra of CSIRO (North Ryde, Australia) [24]. Having also

Table 6.4 Papers from NGC V, SSSC 119 (1998) (Italy)

First author/ reference	Metal	Support	Temperature range/°C	Comments
Hallische [35]	Ni with Co, Ce, Cu or Fe as promoter	α-Al_2O_3	550, 730	Co, Ce, Cu promote activities $H_2/CO>1$
Buarab [36]	Ni	Various supports	600	α-Al_2O_3 most effective support; K poisons reaction
Nichio [37]	Ni	α-Al_2O_3	650–800	Best results for preparation with Ni acetylacetonate
Gronchi [38]	Ni	SiO_2, La_2O_3	600	Pulse reactor study CO_2 reacts with La_2O_3
Provendier [39]	Ni	LaNiFe perovskite	400–800	Perovskite forms Ni–Fe alloy in use. Low coke formation
Kroll [40]	Ni	SiO_2	700	Detailed kinetic study
Kim [41]	Ni	Al_2O_3	600–800	Aerogel catalyst gives low carbon deactivation K addition helpful
York [42]	Ni + W or Mo oxides	Al_2O_3	700	W improves Ni catalyst
	Mo_2C, WC	No support	850	Carbides vs. stable
Suzuki [43]	Ni	$Ca_{0.8}Sr_{0.2}TiO_3$ $BaTiO_3$	850	In situ preparation. Stable against C formation
Stagg [44]	Pt	ZrO_2 with CeO_2, La_2O_3	800	Promoters increase stability and activity
O'Connor [45]	Pt	ZrO_2	600	DRIFTS study; oxidation –reduction mechanism probable
Quincoces [46]	Ni	CaO/SiO_2	650	CaO increases activity
Nam [47]	Ni	Ni–La perovskites with Sr promotion	600–900	Addition of Ca reduces coke formation
Tomishige [48]	Ni	MgO from solid solution	500–850	Addition of small quantities of H_2 stops any deactivation

discussed the various reactions involved and their thermodynamics, these authors gave a very comprehensive review of work on CO_2 reforming published up until 1993. They showed that most of the noble metals and also nickel had been studied and that oxides such as alumina and magnesia had been used as supports for the active metals. They also pointed out that carbon deposition rates seem to depend on the support used and possibly on catalyst morphology, two factors that emerge repeatedly in more recent publications. They mentioned specifically the paper by Gadalla and Somer referred to above [3] in which the use of a Ni/MgO catalyst for up to 125 h was reported; at the end of the experiment, these authors observed only a minute trace of carbon deposition.

Edwards and Maitra also discussed the results of two papers where the activities of a series of metals are reported. In the first, by Takayasu et al. [52], Ni, Ru, Rh, Pt and Pd catalysts supported on "ultrafine single crystal MgO" were compared, the activities being in that order. In the second, by Ashcroft et al. [53], catalysts comprising of Ni, Ir, Rh, Pd and Ru supported on alumina were examined, the order of activity being in the order given. While Takayasu et al. had found that Ru was one of the most active metals, Ashcroft et al. reported that it is one of the least active. (Rostrup-Nielsen has also reported it as being very active [6].) However, both groups found that Ni and Rh are among the most active metals. Listing other papers on the topic, Edwards and Maitra also pointed out that Solymosi et al. [54] and Masai et al. [55] had previously reported that Rh supported on alumina is one of the most active catalysts for the reaction.

Edwards and Maitra closed their review [24] with a discussion of the potential application of thermochemical heat pipe applications for the recovery, storage and transmission of solar energy, showing that the CO_2 reforming reaction can be coupled with the methanation reaction to provide a method of energy transmission (a topic also mentioned briefly by Rostrup-Nielsen in his more extensive review [6]). We return briefly to this topic later (see Table 6.13).

The research papers on CO_2 reforming of methane from the meetings of the Natural Gas Conversion series listed in Tables 6.2, 6.3, and 6.4 cover the use of most of the metal/support combinations that have since been examined in more detail. The vast majority of these papers reported work involving nickel, this being supported on a variety of different oxides, in particular, alumina [6, 25, 27–29, 33, 35, 37, 41, 42], silica [31, 38, 40, 46], magnesia [6], lanthana [30, 38] and zirconia [25]. Some attention was also given to the use of catalysts derived from nickel-containing compounds or from solid solutions of NiO in MgO [48]. Most of the noble metals are also featured, particular attention being focused on Pt [2, 25, 32], Rh [26, 27, 34], Ru [34] and Ir [31], again on a variety of supports. It is interesting to note that there was a wide range in the temperatures of operation, from 400 to 900 °C. As was pointed out above, operation at high temperature is necessary to give acceptably high conversions and so the results at lower temperatures, although giving information on relative activities, have less practical relevance. It should also be noted that the paper by York et al. [42] reports the use of carbides, while the papers by Kikuchi and Chen [33] and Ponelis and Van Zyl [34] both describe the use of membrane systems.

6.4.2 *Highly Cited Publications from the General Literature*

In the following sections, we give a listing of the more significant papers from the recent literature under headings suggested by the brief outline given in the last paragraph. Owing to the very large literature on the subject of CO_2 reforming of methane, the papers selected for mention under each heading are chosen in relation to their citation records, recognising that those papers most frequently referred by

Table 6.5 Some of the most cited reviews on CO_2 reforming listed in the Web of Science

First author/ reference	Comments	Citations (WoS May 2013)
Wang [58]	Identifies areas for future research: effect of metal-support interaction on activity; effects of promoters; reaction kinetics and mechanism; pilot reactor performance and scaleup. Ni on some supports gives carbon-free operation	226
Hu [59]	Reviews catalysts studied, with emphasis on inhibition of C deposition (also reviews partial oxidation)	212
Ross [60]	Review of the development of Pt/ZrO_2 catalysts	134
Ross [61]	General review of CO_2 reforming	59
Bradford [62]	Reviews the use of Ni and Rh catalysts, also single crystals; also partial oxidation	552
Verykios [63]	Review concentrating on the development of Ni/La_2O_3 catalysts. $La_2O_2CO_3$ species are critical to good operation	
Armor [64]	Review largely on steam reforming but also including CO_2 reforming, particularly limitations due to C deposition and also costs of supplying pure CO_2	445
Ma [65]	Review of CO_2 conversion including CH_4 + CO_2 over Ni supported on a wide variety of supports	45
Kodama [66]	Review on production of fuels using sunlight including CO_2 reforming of methane	118

others are likely to be the most important in that field. In the tables, the number of citations to each of the publications given by the Web of Science in May 2013 is shown for comparison purposes; clearly this is only a snapshot of the situation, and it should also be recognised that younger publications will have correspondingly lower numbers of citations than older ones.[5] A reader with a particular interest in one or another type of catalyst would gain an up-to-date picture of the literature on that topic by doing his/her own citation study based on the appropriate key papers listed in the tables.

Table 6.5 lists some of the most cited reviews on the subject of CO_2 reforming. Some of these are very general, covering a whole range of topics from basic aspects to pilot plant results [58], while others are much more focused on one type of catalyst [60, 63]. The review by Armor [64] is of particular interest as it not only covers both steam reforming and CO_2 reforming but also deals with matters such as problems associated with purification of CO_2. Kodama [66] reviews the subject of fuel production using sunlight.

Nickel, although very active for the conversion of methane by either steam reforming or CO_2 reforming, suffers from the problem that it rapidly becomes deactivated by the formation of carbon, this carbon generally being in the form of nanotubes with a nickel crystallite at the tip. Much of the effort has therefore been in trying to find suitable additives for the catalysts that help to minimise this form of carbon deposition, often by modifying the Ni particle size or the support surface in the region of the nickel

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[5] We have paid some attention to this time dependence in our choice of which papers to include.

crystallites. It is now reasonably well established that small nickel crystallites are much less susceptible to C growth, but anchoring the active metal to the support is also known to hinder filament growth. Table 6.6 lists some of the papers reporting the use of catalysts consisting of Ni supported on alumina or modified aluminas. A number of additives are seen to improve the behaviour of the catalysts in relation to the problem of carbon deposition, particularly the alkali [67, 75] and alkaline earth metals [67, 74], lanthana [71] and ceria [68, 73]; ceria is particularly effective.

The effect of reducing the particle size is seen particularly with catalysts based on Ni on MgO; see Table 6.7. This is because the precursor to the active catalyst often involves the formation of a solid solution of NiO in MgO; see, for example, references [77, 80, 83]. Catalysts based on supports such as $MgAl_2O_4$ are also very effective [81–83].

Another support that has received some attention is zirconia, sometimes alone but also often promoted by other species such as ceria [84, 85] or magnesia [83]; see Table 6.8. The effect of Ni particle size on stability has been shown for a zirconia support by Lercher et al. [86]. Other supports studied have included titania [88], lanthana [89], silica [90] and a La–Sr–Ni–Co perovskite [91]; see Table 6.9.

Noble metals have the advantage over Ni in that they do not dissolve carbon, and so the problem of the growth of carbon filaments does not occur with them. As a result, there has been a significant amount of work using catalysts containing noble metals on a variety of supports. Table 6.10 lists some highly cited papers describing the use of supported Pt catalysts on various different supports. Work from this laboratory [60, 95] and also from Bitter et al. [96] has been concerned with the use of Pt on zirconia, this usually being promoted by a small quantity of alumina. Other promoters such as La_2O_3 or CeO_2 are also possible [93].

The other noble metals have also received significant attention, particularly Rh [97–102], Ir [99, 101] and Pd [101, 103]; see Table 6.11. As discussed by Rostrup-Nielsen, a series of successful pilot plant tests have been carried out using a catalyst based on Rh. However, the cost of Rh is prohibitively high so that this work is unlikely to be applied.

Because of the high cost of the noble metals and the resultant problems of operating large scale using them, a significant amount of attention has been paid to the possibility of using MoC_2 or WC as the active component of a catalyst, it being well established that these carbides exhibit properties similar to those of the noble metals. Claridge et al. ([105], see Table 6.12) showed that both of the carbides were active for the reaction, but they reported that there was some evidence of deactivation caused by oxidation of the carbides. Work from this laboratory [106] showed that this was probably due to the fact that the entrance to the CO_2 reforming bed operates under slightly oxidising conditions, this causing the carbide to oxidise, and that the exit part of the bed was stable. The activity of a Mo_2C material supported on ZrO_2 could be improved significantly by promotion with Bi species.

Finally, Table 6.13 lists some references describing work in various laboratories on energy transport systems involving the CO_2 reforming reaction as the endothermic part of the system. It is interesting to note that despite the comments above, the metal of choice for this work appears to be Rh, probably because of the reliable performance far outweighs the disadvantage of cost.

Table 6.6 Some of the most cited papers dealing with Ni supported on Al_2O_3 or modified Al_2O_3

First author/ reference	Metal	Support	Temperature range/°C	Comments	Citations (WoS May 2013)
Horiuchi [67]	Ni	Al_2O_3		Studied effect of adding Na, K, Mg and Ca. All decrease the tendency to deposit carbon	185
Wang [68]	Ni	CeO_2–Al_2O_3		CeO_2 addition (1–5 wt% optimum) gives better activity, stability and C suppression	182
Wang [69]	Ni	Al_2O_3, SiO_2, MgO		Strong metal-support interaction improves stability and coking resistance	129
Kim [70]	Ni	Al_2O_3 aerogel	700	Aerogel supported metal more active and stable than conventional Ni/Al_2O_3 catalyst. C deposition depends on Ni particle size, being significant above 7 nm	154
Martinez [71]	Ni	Al_2O_3		Studies influence of La_2O_3 addition. La decreases rate of coking	79
Juan-Juan [72]	Ni, Ni/K	Al_2O_3	TP reaction to 900, isothermal at 700	Coking rate with K much reduced	59
Laosiripojana [73]	Ni	Al_2O_3–CeO_2	800–900	8 % CeO_2 gives greatly improved behaviour, with greatly decreased C deposition	54
Goula [74]	Ni	CaO–Al_2O_3	750	Ca content influences amounts of C on catalyst after use and also Ni morphology. Origin of C probed by tracer study	90
Osaki [75]	Ni	K–Al_2O_3		K controls Ni ensemble size and thus affects C deposition rates	93

Table 6.7 Some papers dealing with Ni supported on MgO

First author/reference	Metal	Support	Temperature range/°C	Comments	Citations (WoS May 2013)
Rostrup-Nielsen [76]	Ni	MgO		Discussion of all aspects of the reaction over Ni catalysts	674
Tomishige [77]	Ni	MgO, Al_2O_3		Ni0.03MgO0.970 solid solution much more resistant to C deposition than Ni/MgO or Ni/Al_2O_3	239
Wei [78]	Ni	MgO		Careful kinetic analysis (with isotopic measurements) shows C–H bond activation to be sole relevant step	225
Ruckenstein [79]	Ni	MgO and other alkaline earth oxides		Ni/MgO more stable than Ni on the other supports; MgO inhibits Boudouard reaction	194
Ruckenstein [80]	Ni	MgO SiO_2 Al_2O_3	790	Combines CH_4/O_2 with CH_4/CO_2 to decrease chance of explosion. Ni/MgO solid solution catalyst most effective	59
Djaidja [81]	Ni	MgO/Al_2O_3 MgO	800	Ni/MgO sample prepared by co-precipitation less stable than one prepared by impregnation	58
Guczi [82]	Ni	$MgAl_2O_4$		Study of C species formed. Addition of Au shown to improve activity and stop formation of C nanotubes	18
Wang [83]	Ni, Co, Ni–Co	MgAlOx	750	Ni–Co catalyst is very stable; no deactivation after 2,000 h operation. XANES and EXAFS study of catalyst structure	

Table 6.8 Some papers dealing with Ni supported on zirconia

First author/ reference	Metal	Support	Temperature range/°C	Comments	Citations (WoS May 2013)
Roh [84]	Ni	Ce/ZrO_2	750	Work on steam reforming of methane using catalysts previously studied for CO_2 reforming	152
Montoya [85]	Ni	ZrO_2–CeO_2	500–800	CeO_2 stabilises tetragonal ZrO_2. Graphitic C does not cause deactivation. CeO_2 enhances reverse water–gas shift reaction	133
Lercher [86]	Ni, Pt	ZrO_2 and other supports	600, 720–780	Ni/ZrO_2 very stable if low Ni loadings used. (Ni particle size ~2 nm)	94
Nagaraja [87]	Ni	K/MgO–ZrO_2	550–750	Addition of 0.5wt%K increases activity and stability of the Ni/MgO/ZrO_2 catalyst	3

Table 6.9 Some papers dealing with nickel on other supports

First author/ reference	Metal	Support	Temperature range/°C	Comments	Citations (WoS May 2013)
Bradford [88]	Ni	TiO_2 (also SiO_2, MgO)	400–550	Ni/TiO_2 more active than Ni/C, Ni/SiO_2 or Ni/MgO. Ni/TiO_2 suppresses C deposition. Reverse water–gas shift reaction in equilibrium	231, 152
Zhang [89]	Ni	La_2O_3, Al_2O_3, CaO/ Al_2O_3, CaO	750	Sites at Ni–La_2O_3 interface give active and stable performance compared with other supports all of which gave continuous deactivation with time	157
Swaan [90]	Ni	SiO_2	700	Operating catalyst is Ni carbide. Deactivation by catalyst sintering and C deposition	181
Valderrama [91]	Ni–Co	La–Sr–O	600–800	La–Sr–Ni–Co–O perovskite solid solutions give rise to nano-sized crystallites stable under reforming conditions	23

Table 6.10 Some papers dealing with Pt catalysts on various supports

First author/ reference	Metal	Support	Temperature range/°C	Comments	Citations (WoS May 2013)
Ashcroft [92]	Pt and other Pt- group metals	Al_2O_3	400–800	Shows that partial oxidation and CO_2 reforming can be carried out simultaneously	437
Stagg-Williams [93]	Pt	ZrO_2, ZrO_2/La_2O_3, ZrO_2/CeO_2	800	La stabilises support. Ce improves oxygen uptake of support	124
Damyanova [94]	Pt	CeO_2–Al_2O_3	450–600	CeO_2 gives improved Pt dispersion and increased activity. Optimum 1 % CeO_2	118
Ross [60]	Pt	ZrO_2, TiO_2, Al_2O_3	550–800	Pt on ZrO_2 much more stable with respect to C deposition than other samples	130
O'Connor [95]	Pt	ZrO_2, Al_2O_3	550–800	O_2 addition to CO_2 reduces the temperature for a given conversion and also reduces carbon deposition	99
Bitter [96]	Pt	ZrO_2, SiO_2	600–800	ZrO_2 as support activates CO_2, while Pt black or SiO_2 as a support does not	113

Table 6.11 Some papers dealing with catalysts containing Rh, Ru, Ir or Pd

First author/ reference	Metal	Support	Temperature range/ °C	Comments	Citations (WoS May 2013)
Nakamura [97]	Rh	Al_2O_3, TiO_2, SiO_2	277–727	Rh/SiO_2 greatly improved by mixing with Al_2O_3, TiO_2 or MgO	109
Richardson [98]	Rh, Pt/Re	γ-Al_2O_3 washcoated on α-Al_2O_3	Pt–Re deactivates below 700 °C	Foams exhibit high effectiveness factor. Rh best overall catalyst	54
Mark [99]	Rh, Ir	Range of oxides	550–850	Specific rates constant regardless of support. H_2/CO ratio varied by addition of H_2O or O_2	129
Erdohelyi [100]	Rh	Al_2O_3, TiO_2, SiO_2, MgO	150 upwards	Methane adsorbs above 150 °C. Reaction with CO_2 occurs above 400 °C. No carbon deposition observed	29
Erdohelyi [103]	Pd	Al_2O_3, TiO_2, SiO_2, MgO	400–500	Little carbon deposited with stoichiometric gas mixture	127
Qin [101]	Ru, Rh $>$ Ir $>$ Pt, Pd	MgO	600–900	Compares steam and CO_2 reforming. Activity in order shown. Ru, Rh and Ir give little deactivation. Mixed reforming slower	121
Maestri [102]	Rh	Al_2O_3	300–900	Microkinetic analysis of data of Donazzi et al. [104]	44

Table 6.12 Some papers dealing with carbides as catalysts

First author/ reference	Carbide	Support	Temperature range/°C	Comments	Citations (WoS May 2013)
Claridge [105]	Mo_2C, unsupported WC	Al_2O_3, ZrO_2, SiO_2, TiO_2	850–950	Interaction with support during preparation affects activity. Oxidation of carbide causes deactivation	157
Treacy [106]	Mo_2C	Al_2O_3, ZrO_2, SiO_2	950	ZrO_2 material most stable. Addition of Bi gives higher conversions. Catalyst oxidises at entry to bed	2

Table 6.13 Some papers discussing the use of dry reforming as part of an energy transportation system

First author/ reference	Metal	Support	Temperature range/°C	Comments	Citations (WoS May 2013)
Fish [1]	–	–	–	Describes balancing of the reactions for a system including dry reforming (Sandia Natl. Labs.)	27
Levy [56]	Rh	Al_2O_3	750–900	Over 60 cycles of reforming reaction and the reverse (methanation) carried out (Weizmann Institute)	59
Worner [57]	Rh	Foam structures: α-Al_2O_3, SiC	700–860	Both inserts gave some C deposition (Deutch Zentrum Luft und Raumfahrt)	64

6.4.3 Some Recent Publications on CO_2 Reforming of Methane

In conclusion, we list in Table 6.14 a number of recent publications on the subject of CO_2 reforming chosen rather at random from the large number that have been published recently. Many of the themes that we have highlighted above return frequently. While some of the papers report significant improvements in previously described catalyst systems (e.g. [110, 111, 123]), others use the reaction purely as a test reaction (generally at rather lower temperatures) to provide a method of

Table 6.14 Some recent papers (2013) on methane dry reforming

First author/ reference	Metal	Support	Temperature range/°C	Comments
Asencios [107]	Ni	MgO–ZrO_2	750	Coupling of partial oxidation and dry reforming leads to stable operation. Optimum behaviour with 20w% Ni
Zanganeh [108]	Ni	MgO	550–750	Best results with catalyst derived from NiO/MgO solid solution with relatively low Ni content: $Ni_{0.03}$ $Mg_{0.97}O$
Zanganeh [109]	Ni	MgO	700	$Ni_{0.1}$ $Mg_{0.9}O$ samples prepared by surfactant-assisted co-precipitation gave good activities and stabilities (122 h on stream)
Chen [110]	Ni	$CeAlO_3$–Al_2O_3	800	Presence of $CeAlO_3$ phase reduces graphitic carbon deposition; this phase decomposes CO_2 giving active surface oxygen
Xiao [111]	Ni	MgO (ex solid solution)	760	Preparation based on nano-platelets giving homogeneous distribution of the Ni
Bhavani [111]	Ni–Co Ni–Mn	NiCoMnCeZrO and other combinations	800	Mixed $CH_4/O_2/CO_2$ feed. NiCoMnCeZrO gives high activity with little activity loss
Benrabaa [112]	Ni	$NiFe_2O_4$	800	Non-stoichiometric mixed spinel formed under reaction conditions
		$Ni_xFe_{2-x}O_4$		Activity improved by reduction
Gardner [113]	Ni	$Ba_{0.75}Ni_yAl_{12-y}O_{19-\delta}$	900	Activity increases with amount of Ni but C deposition also increases
Baeza [114]	Ni	CaO–La_2O_3–ZrO_2	400–500	CaO (2 wt%) acts as a source of CO and active O species that remove C deposited on surface
Odedairo [115]	Ni	CeO_2	700	Plasma treatment of catalyst gives clean metal–support interface and higher activity and stability than untreated sample

(continued)

Table 6.14 (continued)

First author/ reference	Metal	Support	Temperature range/°C	Comments
Ozkara-Aydinoglu [116]	Ni/Pt	Al_2O_3	580–620	Amount of Pt added has major effect on the reaction kinetics, also on level of inhibition by CO
Tao [117]	Ni	Al_2O_3	700	Sample prepared by single-step surfactant-templating method more active and stable than conventional sample
Ma [118]	Ni	Carbon nanotubes	750	Samples with Ni inside nanotubes more active and stable than those with Ni outside the tubes
Sun [119]	Ni	Mg (and or Ca) O/Al_2O_3	750	NiO/MgO solid solution formed giving active and stable catalyst; CaO addition causes decreased activity and stability
Zhu [120]	Ni	CeO_2/SiO_2	800	Investigation of the effect of calcination atmosphere. Calcination in Ar gives better performance
Albarazi [121]	Ni	CeO_2/ZrO_2/SBA-15	600–800	Promotion of Ni within pores by Ce–Zr–O improves behaviour but gives a decrease in accessibility of the active sites
San Jose-Alonso [122]	Ni or Co	Al_2O_3	700–800	Low metal contents gave low rates of C deposition. Tests for 24 h
Nagaraja [123]	Ni	K–MgO/ZrO_2	550–800	Presence of K^+ incorporated during the co-precipitation of the MgO–ZrO_2 support greatly increases the stability. No C deposition detected with most active and stable samples

characterising a catalyst system (e.g. [116, 121]). One example of an improvement is to be found in work from this laboratory ([123]; see also [87]) that shows that a very stable catalyst with good activity can be achieved with the Ni–Zr–Mg–O system as long as K^+ ions are included in the structure.

6.5 Conclusions

The dry reforming of methane has provided a fertile area of research for more than two decades, and some significant advances have been made in the design of catalysts suitable for the reaction. However, it is at present unlikely that the reaction will be used in practice unless it is combined with either partial oxidation or steam reforming in order to avoid the problems associated with carbon formation. This review has concentrated almost exclusively on the CO_2 reforming of methane, paying little attention to the reactions of other hydrocarbons. However, many of the constraints encountered equally to the reforming of other molecules such as naphtha with the added complication that methane may be formed as a product.

Dedication. The author wishes to dedicate this review to the memory of the late Laszlo Guczi with whom he collaborated in a joint project under the auspices of an ERA-Chemistry project (coordinated by Alain Keinemann) until shortly before his death in December 2012.

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