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Natural gas reforming and CO_2 mitigation

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Abstract

This brief review of work from the author's laboratories summarises work on the steam reforming and CO_2 reforming reactions, discussing some catalysts developed for these reactions. It then presents some work on the use of Mo and W carbides, with and without supports, for the CO_2 reforming reaction, showing that zirconia-supported Mo_2C has some potential for use in the reaction. Finally, the all-over CO_2 balances of a number of reaction sequences for the utilisation of CO_2 are presented, these showing that the production of carbon by a sequence involving CO_2 reforming of methane followed by reduction of CO might be used to remove CO_2 under certain circumstances; the C so produced could either be used as an energy carrier or disposed of.

Keywords: Steam reforming; CO_2 reforming; Pt/ZrO_2 catalysts; W and Mo carbide catalysts; CO_2 abatement

1. Introduction

"Entropy is time's arrow". This, one definition of that rather esoteric quantity, entropy, has been used in the introduction of the concept of spontaneous processes to many generations of undergraduates. All processes producing carbon dioxide are good examples of such spontaneous processes: carbon dioxide is one of the most stable molecules in existence, it being the final product of a sequence of reactions such as the oxidation of a fossil fuel to generate energy. The carbon dioxide formed in combustion processes is, almost without exception, emitted to the atmosphere where it gradually accumulates: a significant contributor to time's arrow. As is now generally recognised, this carbon dioxide functions as a green-house gas, absorbing radiation reflected from the earth and thereby causing a gradual increase in the temperature of the atmosphere. The recognition of the problems likely to arise as a result of the greenhouse effect have lead to treaties aimed at reducing such greenhouse emissions and to much research aimed at identifying means of controlling such emissions.

Carbon dioxide is also formed in other than combustion processes, either as product of the reaction itself or as a by-product. Additionally, when a process is endothermic, energy has to be provided to drive the reaction and this generally requires that a fuel is combusted to provide the energy. A typical example of such an endothermic process is the steam reforming of methane; not only is CO_2 produced in the reaction but the energy required to drive the reaction is obtained by the combustion of methane. There are also several reactions, such as the CO_2 reforming of methane, in which CO_2 is one of the reactants. However, such reactions are highly endothermic and so, as will be discussed in more detail below, additional CO_2 is produced in the energy-producing phase, unless that energy is produced by other means (e.g. using nuclear or solar energy).

This personal review traces research from the author's laboratories on catalysts for the steam reforming of methane and then goes on to review similar more recent work on the CO_2 ('dry') reforming of methane, giving details of several catalyst systems which can be used for these reactions. Although it has been argued that the dry reforming reaction has potential for the mitigation of CO_2, it will be shown that such an application is likely to be largely ineffective, there being a net production of CO_2. Finally, a possible strategy for CO_2 mitigation involving the formation of carbon is presented.

2. The steam reforming reaction

The steam reforming of hydrocarbon feedstocks (reactions (1) or (2) has for many decades been the preferred

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method used industrially for the production of hydrogen either as a pure gas or as a reactant for the production of ammonia or methanol [1]

$$C_nH_{2n+2} + nH_2O = nCO + (2n + 1)H_2 \tag{1}$$

$$CH_4 + H_2O = CO + 3H_2 \tag{2}$$

(Although hydrogen can also be produced electrolytically from water, the electrolytic route has a much lower all-over efficiency and is only used where there is an excess of cheap electricity, for example, where that electricity is produced in hydroelectric systems.) For the reforming process, the feedstock of preference is currently methane (reaction (2)) rather than the naphtha (reaction (1)) used some 40 years ago, methane having the advantage of its higher H/C ratio and its lower tendency to form carbon on the catalysts used. This author's early involvement with the steam reforming of methane was at that time when naphtha was being replaced by natural gas. In our earliest work [2–4], we compared a typical naphtha reforming catalyst (the so-called catalytic rich gas (CRG) catalyst, a very active co-precipitated material originally introduced by British Gas) with a series of supported Ni-alumina materials prepared by impregnation. We showed that active sites involving metallic nickel were important for the former material but that sites formed at the interface between the nickel and the support predominated in the operation of the latter group [2]. In collaboration with the group of L.L. van Reijen in Delft (The Netherlands) [5–7], we examined factors determining the behaviour of the co-precipitated catalysts, showing that the nature of the precipitates formed (hydrotalcites, with characteristic and well-defined layer structures) determined the subsequent behaviours of the catalysts. We then went on to develop a novel catalyst that combined the advantages of the high activities of the CRG catalysts with the mechanical stabilities imparted by α-alumina [8,9]. This was achieved by co-precipitating Ni-alumina hydrotalcite-like precursors in the pores of a preformed α-alumina. We also showed that the catalyst had improved stability and a much greater resistance to carbon lay-down when it was promoted by La ions. The inclusion of La not only increased the specific activity of the Ni but also prevented sintering of the alumina introduced into the pores of the α-alumina matrix [8,10] The catalyst has been in use commercially for some time and is now produced by Johnson Matthey.

3. The development of Pt/ZrO_2 catalysts for reforming and partial oxidation

Following a period during which first methanation [11] and then methane coupling [12] absorbed much attention in the catalysis community, there was at the beginning of the last decade a regeneration of interest in the subject of so-called 'dry reforming', the reforming of methane to syngas using CO_2 as a reactant [13]:

$$CH_4 + CO_2 = 2CO + 2H_2$$

This reaction had been first studied by Fischer and Tropsch in 1928 [14]. In a series of papers in the 1960s, Bodrov et al. (see ref. [15] and other papers from the same laboratory in the same period) had also demonstrated that the steam reforming and CO_2 reforming reactions over Ni materials had very similar kinetics and mechanisms. The reaction is notoriously prone to giving carbon deposition, the chemical potential for carbon deposition for the stoichiometric dry reforming reaction being significantly higher than that in the equivalent steam reforming reaction [1,16]. The renewed interest in the early 1990s arose because several catalysts (e.g. noble metals supported on alumina [17] were reported which were effective for the reaction without exhibiting the serious problems of carbon deposition found with the more conventional catalysts such as Ni supported on alumina. There followed a period of frenzied research activity, somewhat akin to that involving research on methanation during the 1970s or on methane coupling in the 1980s referred to above, in which all conceivable varieties of catalysts were examined for the dry reforming reaction. Many of the associated papers were introduced with the argument that the discovery of an effective catalyst would lead to a solution to the green-house effect, an argument that continued to be used despite the early recognition that, even if the technology could be perfected, the global contribution to the depletion of CO_2 would be minimal unless immense new demands for syngas were generated. Nevertheless, the research led to a new understanding both of the conditions under which dry reforming (or, more realistically, a combination of dry reforming and steam reforming or of dry reforming and partial oxidation) could be carried out and of the catalysts to be used.

The following sections give a somewhat personal review of some of the work which has been carried out in the laboratory of the author on the dry reforming and related reactions over the last decade or so, giving some of the more important results. It is then shown that any reaction of CO_2 to give useful products, whether catalytic or not, cannot be considered in isolation and that the all-over level of removal of CO_2 is significantly lower than that the simple balanced equation implies, this being a result of the demand for energy in the all-over reaction system. Finally, another strategy is put forward which has the potential of sequestering CO_2: the formation of carbon by the reduction of CO with H_2, the mixture having been formed by CO_2 reforming.

3.1. Pt/ZrO_2 catalysts for the CO_2 reforming of methane

Fig. 1 shows the calculated thermodynamic conversion of methane for various CO_2/CH_4 ratios as a function of temperature [18].

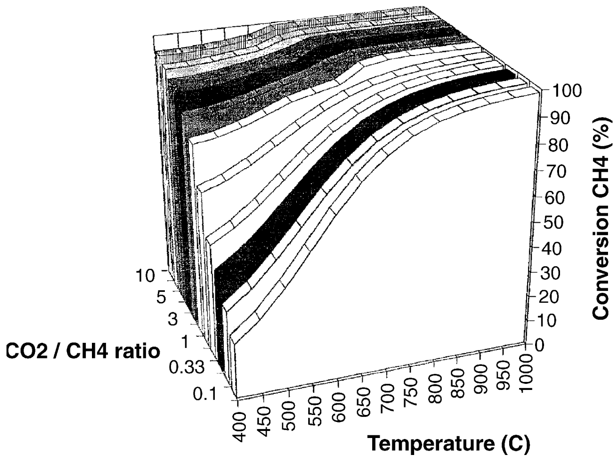

Fig. 1. Thermodynamically calculated conversions of methane as a function of temperature for a series of different feed ratios. Calculations carried out using HSC chemistry (version 1.10, Outokumpu Research, Finland).

Assuming that the ratio chosen for operation will be close to unity, it can be seen that reasonable conversions will only be achieved at high temperatures (above ca. 850 °C). Just as with steam reforming, carbon deposition is a serious problem under most operating conditions. Fig. 2 shows the yield of carbon calculated for a feed ratio of 1:1 of CO_2 to CH_4. It should be noted that the calculations on which this figure is based were carried out assuming a closed system and that the yield of carbon corresponds to the amount of carbon formed for a given conversion of the amounts of methane and carbon dioxide fed; the results must therefore be treated with caution when applied to a continuously fed system and can only be seen as giving an indication of the amounts of carbon which will be formed. The curve with solid points represents the situation if the reverse water–gas shift reaction is at equilibrium:

$$CO_2 + H_2 = CO + H_2O$$

and water is a possible product. The large amount of carbon formed at lower temperatures is therefore a consequence of the occurrence of the Boudouard equilibrium:

$$2CO = C + CO_2$$

If the reverse water–gas shift reaction does not occur, the concentration of CO at lower temperatures is lower and so the level of carbon formation is less (open squares). In both cases, the equilibrium level of carbon formation is lowest at the high temperatures needed to give high methane conversions. However, even at high temperatures, the amount of carbon formed is finite (although lower for the less probable situation in which the reverse water–gas shift reaction does not occur) and so we conclude that carbon formation is possible over the whole range of temperatures. As a consequence, any catalyst suitable for the CO_2 reforming reaction must resist carbon deposition as a consequence of the kinetics of the constituent reactions rather than by a choice of reaction conditions. As it is likely that carbon deposition at the higher temperatures occurs by methane decomposition:

$$CH_4 = C + 2H_2,$$

deposition of massive carbon by this route must be minimised.

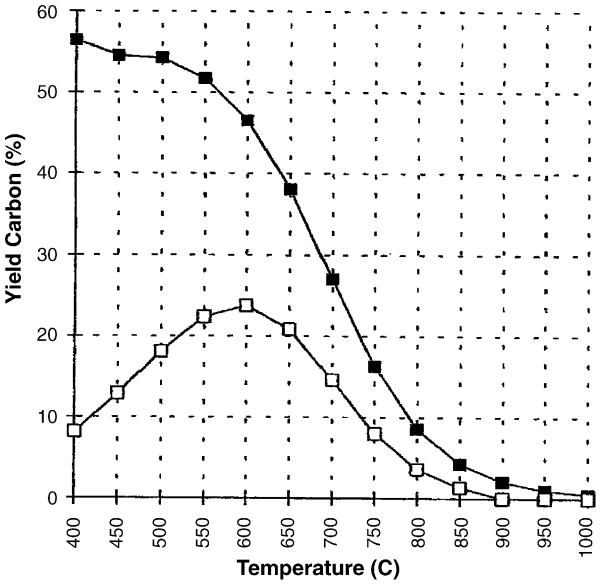

Fig. 2. Thermodynamically calculated proportions of carbon formed under CO_2 reforming conditions with $CH_4/H_2O = 1.0$; (■), with the reverse water–gas shift reaction in equilibrium; (□), without the reverse water–gas shift reaction [18].

The earliest work on CO_2 reforming of methane was carried out using various supported nickel catalysts. As has been shown by Rostrup Nielsen and others [1] in their earlier work on steam reforming, carbon deposition on nickel takes place largely by a mechanism in which carbon atoms formed on the surface of the nickel diffuses through the Ni crystallite to give a carbon filament with a nickel particle on the top. The growth of these filaments causes an expansion of the catalyst particles and this often then results in either the breakdown of the preformed catalyst particles (e.g. pellets or extrudates) or blockage of the bed by carbon, or both together. Encapsulation of the nickel by carbon can also occur under certain circumstances and this causes blockage of the exposed nickel surfaces and deactivation (i.e. poisoning) of the catalysts. Reaction conditions for nickel catalysts are therefore generally chosen to be well outside those required thermodynamically for carbon formation. In the case of steam reforming, this requires for safety reasons (to prevent reactor blockage) that a plant be operated at steam/carbon ratios which are significantly higher than those required thermodynamically. This has major consequences in terms of the economics of plant operation as it involves substantial recycling of steam. (In passing, it is perhaps worth noting that one of the reasons for the success of the Ni-Al-La catalyst described above [8,9] is that it is able to resist

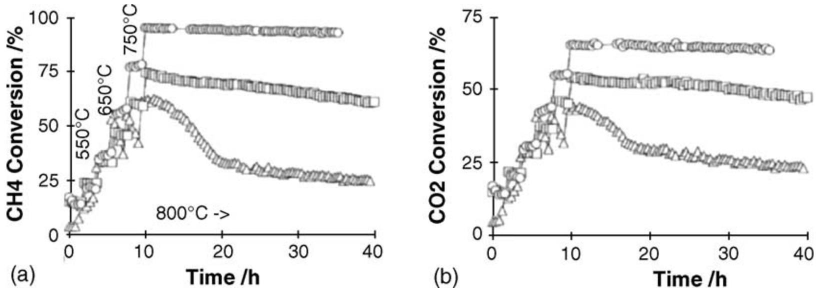

Fig. 3. Plots of (a) methane conversion and (b) CO_2 conversion as a function of time at various temperatures for 1 wt.% Pt supported on alumina (△), titania (□) and zirconia (○); $CO_2/CH_4 = 2.0$; GHSV = 28,000–34,000 h^{-1}. (*Reproduced with permission from Studies in Surface Science and Catalysis* 107 (1997) 537–546).

massive carbon deposition under conditions of plant malfunction, e.g. loss of steam partial pressure, as the strong α-alumina matrix does not fragment under conditions of carbon laydown and so carbon deposition is limited by the geometric size of the pores.)

As indicated above, the work of Ashcroft et al. [17] on the CO_2 reforming reaction demonstrated that it was possible to use noble metals such as Ir supported on alumina for the CO_2 reforming reaction. However, their paper showed that Pt supported on alumina was not an effective catalyst for the reaction due to serious carbon deposition. As is demonstrated by the results shown in Fig. 3, we found that Pt supported on zirconia was superior to equivalent Pt on alumina or Pt on titania materials [19]. There was a significant drop with time of the activity at each of the temperatures studied of the alumina-supported catalyst compared with the zirconia one, presumably due to more significant carbon deposition in the former case. The behaviour of titania material was intermediate between the other two.

We also examined the behaviour of different noble metals supported on zirconia and the results are shown in Fig. 4. In these experiments, the temperature was increased in a series of steps and in several cases there was a gradual increase or decrease in conversion with time. The Rh and Pt materials were the most active over the whole temperature range while the Ir, Pd and Ru catalysts were much less active. As discussed in reference [19], the orders differ from those given by Ashcroft et al. for alumina-supported metals [17] and by Rostrup Nielsen and Hansen [20] and by Qin and Lapzewich [21] for magnesia-supported metals. Taking into account the dispersions of the Rh and Pt (91 and 84%, respectively) and the actual loadings and atomic weights of the metals (1.3 and 0.9 wt.% and 107 and 195, respectively), the turnover number of the Rh catalyst was actually significantly lower than that of the Pt material. (It should be noted that the actual experimental sequence used for the comparison of the materials is of some importance as the deposition of carbon at the lower temperatures with some of the metals in these experiments may have had an effect on the activities at higher temperatures. However, experiments in which tests were carried out only at the higher temperatures gave similar results.)

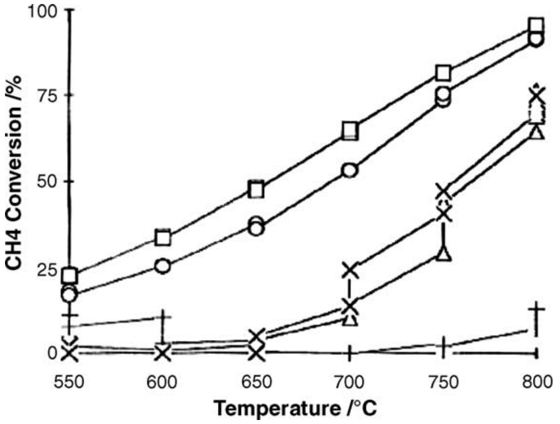

Fig. 4. Plots of CH_4 conversion as a function of temperature for a series of ZrO_2-supported noble metals with approximately 1 wt% metal: (□), Rh; (○), Pt; (△), Ir; (×), Pd; (+), Ru. The reaction conditions are the same as those shown in Fig. 3 (*Reproduced with permission from Studies in Surface Science and Catalysis* 107 (1997) 537–546).

Experiments were then carried out to determine the optimum Pt loading for the Pt/ZrO_2 material and it was shown that the results for 0.5 and 1.0 wt.% were similar. Further work on optimising the catalyst was therefore carried out using the lower loading. Fig. 5 shows the results of a longer term experiment in which the Pt was supported on ZrO_2 extrudates containing a small quantity of alumina to give mechanical strength. It can be seen that although the

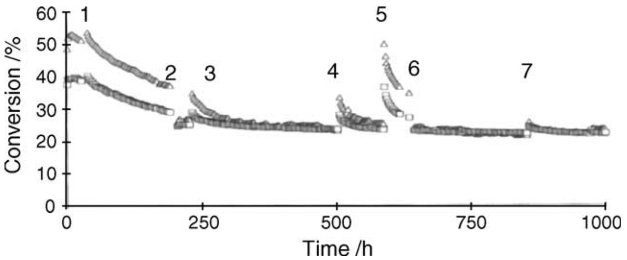

Fig. 5. CH_4 and CO_2 conversions as a function of time on stream for a 0.5 wt.% Pt/ZrO_2 catalyst. The temperature over the length of the catalyst bed was 650–700 °C; GHSV = 16,000 h^{-1}, $CO_2/CH_4 = 2.0$. See text for details of 1–7. (*Reproduced with permission from Studies in Surface Science and Catalysis* 107 (1997) 537–546).

conversions of methane and CO_2 both decreased with time, the catalyst still gave significant conversions after 1000 h of operation. At points 1, 3, 4 and 7, one or other gas was replaced and the feed gas by-passed the reactor for some time; the activity of the catalyst after renewing the gas stream had in each case increased and, the CO_2 being in excess, it was therefore concluded that carbon was removed from the active surface by the reverse Boudouard reaction:

$$C + CO_2 = 2CO$$

Exposure to a stream of CO_2 alone (point 5) gave an even more marked effect, the subsequent conversions reaching values not far different to those for the fresh catalyst. It is interesting to note that the reactivated catalyst after each excursion deactivated more rapidly than the fresh material. Point 2 corresponds to a short period at 100 °C and point 6 corresponds to a short period at between 200 and 300 °C. Both temperature excursions appeared to bring about increased rates of deactivation, possibly corresponding to the deposition of Boudouard carbon at the lower temperatures.

3.2. *Pt/ZrO_2 catalysts in related reactions and a mechanistic model for CO_2 reforming*

Further work [22] showed that the Pt/ZrO_2 catalyst could also be used for partial oxidation and that a combination of partial oxidation and CO_2 reforming could also be carried out. As shown in Fig. 6, this could allow control of the H_2/CO ratio achieved, this ranging from just below 1.0 for pure CO_2 reforming (some reverse water–gas shift occurring under the conditions used) to 2.0 for partial oxidation alone.

Temperature profiles measured in the catalyst bed also showed significant advantages to operating the catalyst with a mixture of CO_2 and O_2: with pure CO_2, there was a distinct endotherm at the beginning of the bed, with pure O_2, there was a large exotherm at the beginning of the bed (corresponding to methane combustion) while with combinations of CO_2 and O_2, there were a much more even temperature profiles. It was also shown gravimetrically that while there was measurable carbon deposition during CO_2 reforming (up to what corresponded to approximately a monolayer on the Pt surface), no measurable carbon deposition occurred in the presence of oxygen. There was also evidence in experiments carried out with cycles of CH_4 and CO_2 for the occurrence of slight reduction of the zirconia support when exposed to CH_4 and subsequent re-oxidation when exposed to CO_2 [23]. This led to the postulation of the oxidation–reduction mechanism depicted in Fig. 7.

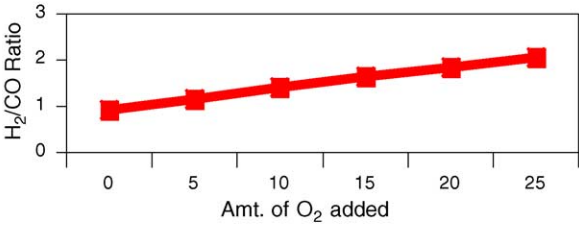

Fig. 6. H_2/CO ratios obtained for a series of experiments carried out with a Pt/ZrO_2 catalyst at 800 °C using different feeds ranging from pure CO_2 to pure O_2 [22]. Sum of $CO_2 + O_2$ flow rates = 25 $cm^3\ min^{-1}$; the C/O ratio was maintained at 1.0 by increasing the CH_4 flow as the O_2 flow was increased.

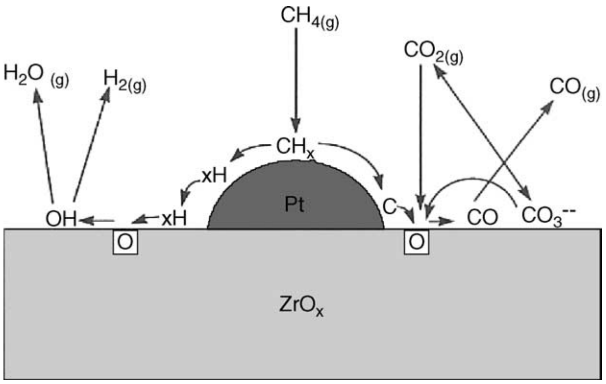

Fig. 7. A model for CO_2 reforming of CH_4 over a Pt/ZrO_2 catalyst. (*Reproduced with permission from Studies in Surface Science and Catalysis* 119 (1998) 819–824).

In this, a molecule of methane reacts at the Pt surface to give carbon species and hydrogen is desorbed. Some of the carbon accumulates on the surface of the Pt crystallite but some diffuses to the interface between the Pt and the zirconia support where it picks up an oxygen from the support and desorbs as CO. The oxygen of the support is then replaced by the reaction of a molecule of CO_2 with the desorption of a further molecule of CO. This model can be extended to explain the results quoted above for the partial oxidation situation. In that case, the oxygen also adsorbs at the Pt surface and then preferentially attacks any carbon atoms on the Pt. Hence, carbon does not accumulate on the surface during mixed reforming.

Additional work showed that the Pt/ZrO_2 catalyst could be used successfully for the $CH_4 + H_2O$ reaction under conditions that would normally give rise to carbon deposition and that mixtures of CO_2 and steam could also be used to give a range of H_2/CO ratios [19], as shown above for the mixed partial oxidation and CO_2 reforming. The scheme shown in Fig. 7 also allows for steam reforming; if water is added to the system, it can also be used to re-oxidise the partially reduced zirconia support with the liberation of hydrogen. It should be noted that the model also explains why the addition of a variety of promoters to the zirconia such as La or Y improves the behaviour of the resultant catalysts [24]: these encourage the oxidation–reduction of the support. It is therefore also not surprising that the addition of CeO_2 to the support enhances the behaviour of the resultant catalyst, the ceria being a source of additional labile oxygen species [25,26].

The recognition that the Pt/ZrO_2 catalyst appeared to bring about the water–gas shift reaction to equilibrium under all the conditions we had used for the various reforming reactions led us to examine the behaviour of these materials as water–gas shift catalysts [27]. We found that the catalyst had an activity for the reaction which was intermediate between that of a commercial Cu-containing low-temperature shift catalyst and a commercial Fe/Cr high-temperature shift catalyst. The catalyst could be used without any significant deactivation with stoichiometric reaction mixtures. The catalyst was also very effective for methane combustion [28], having an activity under typical reaction conditions close to that exhibited by a commercial $Pt\text{-}SnO_2\text{-}Al_2O_3$ material. When promoted with SnO_2, the activity and stability was far superior to that of the alumina-supported material.

4. Carbides as substitutes for supported metal catalysts

As yet, apart from a pilot plant operating the so-called SPARG process using sulphur-passivated nickel catalysts [29], there have been no commercial applications of the CO_2 reforming process. This is seemingly partly as a result of there being little demand for a process producing low H_2/CO ratios but particularly as a result of a reluctance to operate a plant under conditions which thermodynamically favour carbon deposition. Although the Pt/ZrO_2 catalysts described above seem to offer a solution to the latter problem, there is a reluctance to apply them for two reasons: the potential mechanical instability of the support material due to phase changes in the temperature range in which the catalyst operates; and the high cost of the Pt even at loadings of 0.5 wt.%. While the former problem may be overcome by stabilising the zirconia by the addition of a species such as yttrium (with the added advantage that the Y increases the ability of the support to supply oxygen), the cost factor appears currently to mitigate against the use of Pt/ZrO_2 or equivalent materials. Green and his co-workers [30–32] have recently shown that it is possible to use several carbides as substitutes for supported metals as catalysts for dry reforming. We have examined the use of these carbides for dry reforming and have shown that the carbides only maintain their activities under conditions when the carbide is stable in the presence of the CO_2 of the reaction mixture and that requires there either to be back-mixing or some other way of ensuring that there is CO present at the beginning of the bed [33,34]. Taking WC as an example, the equilibrium to be considered is:

$$WC + 3CO_2 = WO_2 + 4CO$$

Assuming that the water–gas shift reaction is at equilibrium throughout the bed, it was possible to calculate the CO_2/CO ratios occurring in the bed at different CH_4 conversions at different temperatures and total pressures for a number of carbides. Only the carbides of W and Mo show any range of stability but both are unstable at low methane conversions. These conclusions were borne out by examination of the material at the beginning and end of a used bed using XRD and Raman spectroscopy.

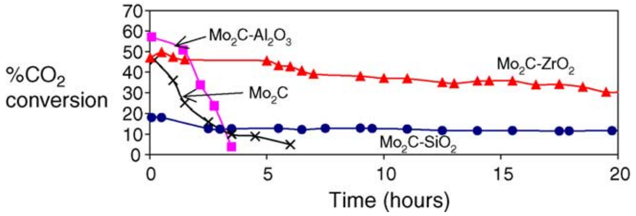

Fig. 8. CO_2 reforming of CH_4 using: (1) Mo_2C; (2) 5 wt.% $Mo_2C\text{–}Al_2O_3$; (3) 5 wt.% $Mo_2C\text{–}ZrO_2$; and (4) 5 wt.% $Mo_2C\text{–}SiO_2$. [950 °C, $CO_2/CH_4/N_2$: 50/50/5 ml/min, 0.33 g catalyst].

Fig. 8 shows some typical results obtained for the CO_2 conversions as a function of time for a Mo_2C sample (crosses) and also for a series of supported materials. It can be seen that the unsupported material loses almost all of its activity over a period of about 3 h. However, when the Mo_2C was supported on a range of supports, the stability of the catalysts was greatly improved, this being particularly the case for the case of zirconia. It would appear that the zirconia is again acting as a very good support and that it is stabilising the active phase (which may or may not be a molybdenum carbide species – it may also be a stable polymolybdate species which is not converted to a carbide under normal carbiding conditions). A critical parameter is also the temperature at which the material is calcined prior to carburisation, a temperature of 400 °C giving better results than one of 600 °C.

The effect of adding various promoters to the catalyst was also examined and the results are compared in Table 1. It can be seen that when Bi was added as a promoter, the activity of the catalyst was considerably increased. It would appear that this improvement is due in some way to the improved dispersion of the Mo species on the support surface, perhaps due to the formation of Bi molybdate species in the precursor. Further work needs to be done to gain a greater understanding of the nature of the active phase formed with such materials (are they really carbides or does the surface

Table 1

Conversions obtained in CO_2 reforming of CH_4 using: (1) 5 wt.% $Mo_2C\text{–}ZrO_2$; (2) 5 wt.% Mo_2C–1 wt.% $Ni\text{-}ZrO_2$; (3) 5 wt.% Mo_2C–1 wt.% $Bi\text{-}ZrO_2$; and (4) 5 wt.% Mo_2C–1 wt.% $Co\text{-}ZrO_2$, [950 °C, $CO_2/CH_4/N_2$: 50/50/5 ml/min, 0.33 g catalyst]

Mo phase	Promoter	Support	% CO_2 conversion
Mo_2C	–	ZrO_2	58
Mo_2C	Bi	ZrO_2	74.6
Mo_2C	Ni	ZrO_2	59.4
Mo_2C	Co	ZrO_2	55.6

All catalysts were calcined at 400 °C prior to carburisation rather than at 600 °C for the data shown in Fig. 8. The results were recorded after 3 h of testing.

molybdate species resist carburisation and have an activity of it own?) and to see if other promoters can improve the behaviour still further. It should, however, be noted that the activities of these 'carbide' catalysts are significantly lower than those of the supported noble metals as the temperature required to give adequate conversions are some 100 °C higher for the carbides than for the supported noble metals.

5. CO_2 reforming and CO_2 mitigation

As indicated above, many papers on the subject of CO_2 reforming include reference to the possibility of using CO_2 reforming of methane as a method of reducing CO_2 emission to the atmosphere. It is however unlikely that any such approach will ever be used since the amount of CO_2 emitted very greatly exceeds the amount of potential products that might be made. For example, the syngas made in the reaction could be used for the production of Fischer Tropsch fuels or of methanol (and both would require an adjustment of the CO/H_2 ratio of the syngas using for example the water–gas shift reaction). However, in both these cases the reaction would only give a temporary storage of the CO_2 since both products are likely to be used ultimately as fuels; if the methanol was not used as a fuel and only current markets were supplied, the use of CO_2 would only be a small fraction of 1% of world production of CO_2. However, even in such estimates, an important factor seems to be ignored, the fact that a number of the steps in such reactions are endothermic and that energy has to be supplied to make them occur. In practice, this energy is likely to be supplied by combustion of natural gas, thereby contributing further CO_2 to the all-over balance. (These arguments, of course, will not apply if the energy is supplied from renewable or other non-fossil sources. For example, the use of energy from a nuclear reactor [35] or from solar energy can be considered.) If the endothermic CO_2 reforming reaction alone is carried out, the all-over enthalpy change required to make the reaction to go to completion is +261 kJ(mol CO_2)$^{-1}$. This would normally be supplied by the combustion of methane ($\Delta Ho = -800$ kJ(mol CH_4)$^{-1}$). If we assume that the efficiency of heat transfer is approximately 80% (and this is probably optimistically high), then approximately 0.4 moles of CO_2 will be produced for every mole of methane or CO_2 consumed in the reforming process. Hence, the total loss of CO_2 is only 0.6 moles and the total consumption of methane is 1.4 moles. When CO_2 reforming is used to provide syngas for other processes, the all-over consumption of CO_2 will depend on the energetics of the subsequent processes: if the process is exothermic (and most consuming syngas are), some energy can be fed back to the reforming step. We have carried out some very approximate calculations based on the all-over energetics of several reactions which might be used to consume CO_2, the energy required for the reaction again being provided by the combustion of methane. The results of these calculations are presented in Table 2. It can be seen that the production by a Fischer Tropsch process of one molecule of C_6H_{12} (chosen for convenience of balancing equations to give a C_6 hydrocarbon) consumes 95% of the CO_2 given in the all-over balanced equation while the production of one molecule of methanol uses only 66% of the CO_2 for the balanced equation. However, a third possibility, the production of carbon by the reduction of CO (which would require the production of syngas at high temperature and the subsequent reduction of the CO at low temperatures) is a thermally neutral reaction and would therefore offer a method of mitigating 100% of the CO_2 required in the balanced all-over equation:

$$CH_4 + CO_2 \rightarrow 2C + 2H_2O + 12.5\ \mathrm{kJ}$$

Table 2
The all-over energetics of the conversion of CO_2 to several products

Route	Moles of CO_2 mitigated per mole of CO_2 consumed	Conclusions
CH_4 to higher hydrocarbons (CH)		
Reactions $CH_4+CO_2 \rightarrow 2CO + 2H_2$ $CH_4+H_2O \rightarrow CO + 3H_2$ $6CO + 13H_2 \rightarrow C_6H_{12}+H_2O$ All-over reaction $4.5CH_4 + 1.5CO_2 + 3H_2O + 27\ \mathrm{kJ} \rightarrow C_6H_{12} + 6H_2O$	A net reduction of 0.95 moles of CO_2	This is an effective method of CO_2 mitigation. However, the diesel produced will subsequently be burnt in an engine → short term CO_2 fixation
CH_4 to methanol		
Reactions $CH_4+CO_2 \rightarrow 2CO + 2H_2$ $CH_4+H_2O \rightarrow CO + 3H_2$ $CO + 2H_2 \rightarrow CH_3OH$ All-over reaction $3CH_4 + CO_2 + 2H_2O + 175\mathrm{kJ} \rightarrow 4CH_3OH$	A net reduction of 0.66 moles	Provides a trap for some CO_2. If methanol production was shifted to a process which used combined CO_2 + steam reforming then global CO_2 emissions would be reduced by only 0.0027%
CH_4 to carbon		
Reactions $CH_4+CO_2 \rightarrow 2CO + 2H_2$ $2CO + 2H_2 \rightarrow 2C + 2H_2O$ All-over reaction $CH_4 + CO_2 \rightarrow 2C + 2H_2O + 12.5\ \mathrm{kJ}$	A net reduction of 1 mole	Offers an energy efficient means of CO_2 mitigation. Carbon can be used as adsorbent or as catalyst support. Excess carbon can be easily dumped or disposed of

This reaction would, however, consume one molecule of natural gas per molecule of CO_2 used and so the reaction would only be feasible in situations where natural gas was available at negligible or even negative cost, for example, at remote hydrocarbon fields where the gas would normally be flared or returned to the wells. In this case, the carbon formed could either be stored or transported to locations where it could be utilised, e.g. as an adsorbent or for the production of syngas or hydrogen by the reverse of the reaction used to form the carbon (Table 2):

$$C + H_2O = CO + H_2$$

and the subsequent water–gas shift reaction:

$$CO + H_2O = CO_2 + H_2.$$

This is thus the equivalent of transporting two molecules of hydrogen per molecule of carbon. The transportation of the carbon is likely to be more economical than the transportation of the natural gas as no refrigeration or pressurisation would be required—although the carbon would have to be blanketed by an inert gas to prevent spontaneous combustion. Any catalyst used for the reaction to form the carbon would be transported with it and would also be used for the reverse reaction.

6. General conclusions

The production of syngas from natural gas (and also of other hydrocarbons) can be achieved by a number of different reactions. The best established of these is steam reforming, this giving an H_2/CO ratio of 3.0, the ratio being then adjusted as required by using the water–gas shift reaction. CO_2 ('dry') reforming gives rise to a syngas ratio of 1.0, this being that required for a small number of processes. For gas-to-liquids technology, the required ratio is 2.0 and most attention is being given to partial oxidation as a means of achieving this. However, a combination of steam and CO_2 reforming is also possible for such purposes. This personal review traces some work of the author and a large number of his colleagues on some of these reactions, with particular attention to the use of zirconia-supported noble metals and carbides for the dry reforming reaction. It would appear that the use of zirconia as a support in such reactions offers considerable benefits compared with the use of other supports, apparently as a result of the ability of the zirconia to take part in the reactions involving CO by an oxidation–reduction mechanism. Clearly, there is room for much more work on such systems and on the inclusion of other additives to improve the properties of such catalysts still further since they appear to be among the best examined to date for operation under conditions in which carbon deposition is thermodynamically permissible. The review ends with a brief consideration of the all-over energetics of several reactions from which it concluded that dry reforming followed by CO reduction might offer a method of CO_2 mitigation.

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