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Recent advances in the conversion of methane to synthesis gas

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Abstract

A brief review on the recent developments of alternative routes for synthesis gas production, namely catalytic methane partial oxidation and methane reforming with carbon dioxide, is presented. Particular attention is given to reaction thermodynamics, catalyst formulation, reaction mechanism and problems of carbon deposition.

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1. Introduction

This article is concerned with processes for the conversion of methane to carbon monoxide and hydrogen. The three reactions that attract industrial interest are: the methane steam reforming reaction (1), methane partial oxidation with oxygen or air (2) and methane dry reforming with carbon dioxide (3).

$$CH_4 + H_2O = CO + 3H_2 \quad \Delta H = +226\ \mathrm{kJ\ mol^{-1}} \qquad (1)$$

$$CH_4 + \tfrac{1}{2}O_2 = CO + 2H_2 \quad \Delta H = -44\ \mathrm{kJ\ mol^{-1}} \qquad (2)$$

$$CH_4 + CO_2 = 2CO + 2H_2 \quad \Delta H = +261\ \mathrm{kJ\ mol^{-1}} \qquad (3)$$

The first detailed study of the catalytic reaction between steam and methane was published in 1924 [1]. It was subsequently found that many metals including nickel, cobalt, iron and the platinum group metals could catalyse reaction (1) to thermodynamic equilibrium [2,3]. Nickel catalysts emerged as the most practical because of their fast turnover rates, long-term stability and cost. The major technical problem for the nickel catalysts is whisker carbon deposition on the catalysts, which can lead to the plugging of the reformer tubes. It was found that carbon deposition could be substantially reduced by the use of an excess of water and a temperature of about 1073 K. Under these conditions carbon formation is thermodynamically unfavourable. The unreacted water is separated from the product synthesis gas and recycled. In the 1930's this combination of high equilibrium synthesis gas yield and the ready availability of natural gas resulted in the rapid development of this technology for the industrial conversion of natural gas into synthesis gas. Indeed, the first steam reforming plant was commissioned in the early 30's [4] and many industrial steam reforming plants were subsequently built throughout the world. It is still the most important industrial process for the production of carbon monoxide and hydrogen. However, there are drawbacks to this process. First, superheated steam (in excess) at high temperature, is expensive, secondly the water–gas shift reaction produces significant concentrations of carbon dioxide

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in the product gas and thirdly, the H_2-to-CO ratio is higher than the optimum required for the downstream synthesis gas conversion to methanol, acetic acid or hydrocarbons. In the case of Fischer–Tropsch synthesis, high H_2/CO ratios limit the carbon chain growth.

The alternative reactions for synthesis gas production, namely partial oxidation using oxygen (2) and dry reforming with carbon dioxide (3), both give lower H_2/CO ratios but they have received much less attention. The mildly exothermic partial oxidation of methane to synthesis gas was first investigated in the 30's and 40's [5–7] but, at the stoichiometric methane-to-oxygen ratio used, carbon formation occurred on the metal catalysts. Such undesirable carbon formation cannot be avoided by increasing the oxygen-to-methane ratio or by increasing the operating temperature without also increasing the potential explosion hazards, separation problems, gas phase reactions and decreased synthesis gas selectivities. Catalytic partial oxidation has thus been virtually ignored for the last 50 years. It was not until the recent oil crisis that there was renewed interest in the conversion of methane, which is the principal component of natural gas. Green and co-workers reported in 1990 that some noble metals could, on a laboratory scale, catalyse methane partial oxidation to the thermodynamic equilibrium composition of product gases with little or no carbon deposition [8,9]. This observation reawakened industrial and academic interest in the catalytic partial oxidation of methane to synthesis gas. The recent developments in the catalytic partial oxidation of methane and the closely related methane dry reforming reaction are discussed below.

2. Methane partial oxidation: reaction thermodynamics

Reaction of CH_4 with O_2 at high temperatures gives principally CO, CO_2, H_2O and H_2. The composition of the product gas depends on temperature, pressure, input gas composition, and also on kinetic factors. The important reactions occurring in partial oxidation are:

$$CH_4 + 2O_2 = CO_2 + 2H_2O \qquad (4)$$

$$CH_4 + 1\tfrac{1}{2}O_2 = CO + 2H_2O \qquad (5)$$

$$CH_4 + O_2 = CO_2 + 2H_2 \qquad (6)$$

$$CH_4 + H_2O = CO + 3H_2 \qquad (7)$$

$$CH_4 + CO_2 = 2CO + 2H_2 \qquad (8)$$

$$CO + H_2O = CO_2 + H_2 \qquad (9)$$

The calculated thermodynamic gas compositions at various temperatures, based on the above reactions, at 1 atmosphere pressure and with an input methane-to-oxygen (air) ratio of 2:1 are shown in Fig. 1. It can be seen that as the temper-

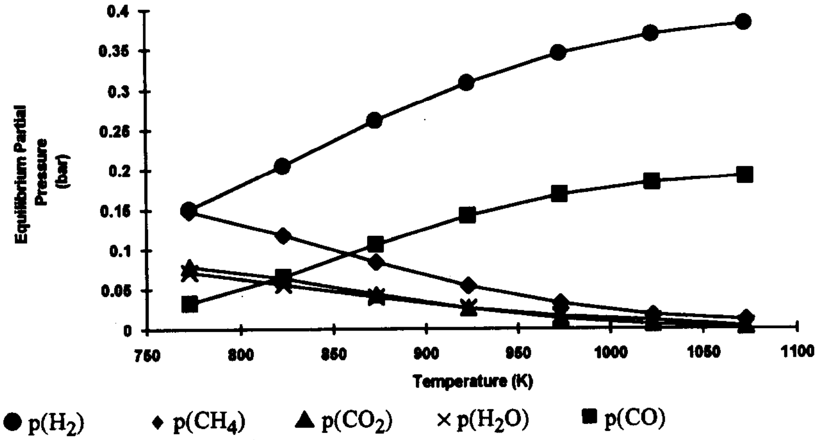

Fig. 1. Equilibrium gas compositions for partial oxidation, 1 bar, 2:1 CH_4:O_2 (as air).

Table 1
Table 1 Effect of flow-rate on the catalyst-bed temperature

F/W (ml g^{-1} h^{-1})	CH_4 conv. (%)	CO sel. (%)	H_2/CO	CO yield (%)	Catalyst bed temp. (K)
2.5x 10^4	31.0	25.8	8.3	8.0	ca. 723
5.2x 10^5	76.0	80.5	2.1	61.2	1046
5.2x 10^5 [a]	73.0	82.0	2.0	59.9	?

Catalyst = Ni/MgO (3:1 Ni:Mg), $CH_4/O_2 = 2$, furnace temperature = 723 K. A further thermocouple is inserted directly into the catalyst bed.
[a]Ref. [11].

ature increases so also does the selectivity to CO and H_2, for example, at 773 K, the equilibrium gas composition is calculated to be 0.032 bar CO; 0.078 bar CO_2, 0.149 bar CH_4 and 0.151 bar H_2. At 1023 K, this changes to values of 0.1830 bar CO, 0.006 bar CO_2; 0.017 bar CH_4 and 0.369 bar H_2. Therefore, very high methane conversion (>90%) and selectivity (>90%) to synthesis gas can be obtained above 1000 K.

Lunsford and co-workers [10] have also calculated the equilibrium concentrations of product gases at various pressures. Their data indicate that methane, carbon dioxide and water concentrations increase at high pressures. However, increasing the reaction temperature can compensate for the effect of pressure. For example, methane conversions greater than 80% with more than 90% selectivity to CO are predicted above 1173 K at total pressures of 10 bar. Thus, by analogy with methane steam reforming, the production of synthesis gas from CH_4/O_2 mixtures is thermodynamically feasible at the elevated pressures preferred for commercial operation.

However, carbon deposition which is thermodynamically favourable should also be considered in the above calculations, namely the formation of carbon by the Boudouard reaction, Eq. (10), or by catalytic methane decomposition, Equation. (11).

$$2CO = C + CO_2 \qquad (10)$$

$$CH_4 = C + 2H_2 \qquad (11)$$

The equilibrium constants for both these reactions [3] lie substantially above the values calculated for the exit gas compositions for the lower temperature range. Thus, under the stated conditions carbon formation is thermodynamically favourable below about 1200 K.

Recently, Choudhary and co-workers have reported that high yields and selectivities to synthesis gas (>85% selectivity) can be obtained over nickel [11–14] and cobalt [15,16] supported on various oxides under conditions of apparently low temperature, (723–773 K) and very short residence times. The thermodynamic calculations at these temperatures predict that CO selectivity would be much lower than their results (Fig. 1). They also observed low conversions for steam and dry reforming of methane over the same catalysts at the same reaction conditions. They suggested that a process giving high selectivity to synthesis gas is occurring under *non-equilibrium* conditions and there is a reaction path completely different from that of the equilibrium processes. However, Chang and Heinemann [17] have reexamined Co/MgO for methane partial oxidation and found that catalysts with high cobalt content were able to initiate the reaction of methane with oxygen at temperatures of around 773 K. High conversions of methane (about 70%) and very high selectivities for hydrogen and carbon monoxide (about 90%) were also obtained at high reactant gas space velocities. They found, using an infrared radiation thermometer, that the catalyst temperatures during methane partial oxidation to synthesis gas were actually extremely high (1473–1573 K) even though the furnace was at 773 K.

We have investigated the Ni/MgO catalyst described by Choudhary. The effect of flow-rate on the catalyst-bed temperature was investigated and the data are shown in Table 1 and Fig. 2. The

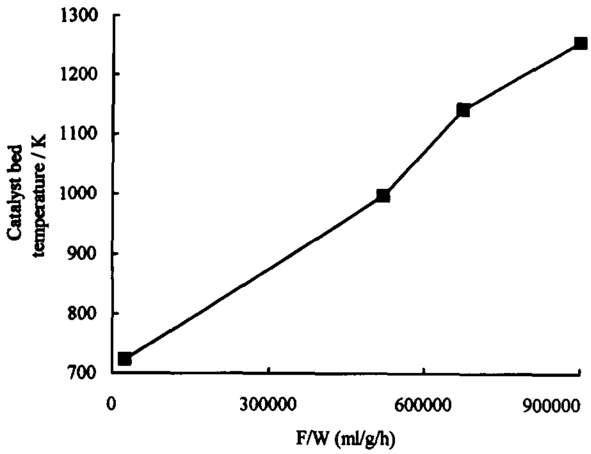

Fig. 2. The effect of flow-rate on the catalyst-bed temperature using the Ni/MgO (Ni/Mg = 3) catalyst. Furnace temperature = 723 K, $CH_4/O_2 = 2$.

typical flow-rate reported by Green and co-workers [9] corresponds to the first point on the graph, where only 25.8% selectivity to CO is obtained over this catalyst at 723 K. This conversion and selectivity agree with the thermodynamically predicted values. Using the conditions described by Choudhary and co-workers, namely the same temperature but at high flow-rates ($> 5 \times 10^5$ ml g^{-1} h^{-1}), it was found that the catalyst temperature increased to > 1000 K, as shown in the Fig. 2. Since exothermic combustion reactions generate heat in the catalyst bed, the temperature can substantially increase when higher space velocities are used (adiabatic conditions). Similar results were obtained by Lunsford and co-workers for Ni/Yb_2O_3 catalysts [19], which may account for Choudhary's observations.

3. Survey of the various metal-containing catalysts used for partial oxidation

It is well-established that the partial oxidation of methane to synthesis gas occurs at very high temperatures (> 1400 K), as for example in a flame [20]. The use of a catalyst can bring down the operating temperature necessary to achieve thermodynamic equilibrium. As shown in Fig. 1, high yields of synthesis gas can be obtained at temperatures of about 1023 K if the system reaches equilibrium. Catalysts containing many different transition metals have been described in the literature.

3.1. Ni, Co and Fe catalysts

Since the first report of the partial oxidation of methane (input $O_2/CH_4 = 1/2$) by Prettre et al. [6] supported nickel catalysts have been studied in detail. The nickel catalyst used by Prettre et al. [6] gave high yields of 2:1 H_2/CO synthesis gas at temperatures between 1000 and 1200 K at 1 atmosphere. They proposed that a sequence of reactions including methane total oxidation reactions and reforming reactions (reactions 4–8) was taking place over their nickel catalysts. The calculated equilibrium gas composition based on those reactions gave good agreement with the observed exit gas compositions, which implied thermodynamic equilibrium had been established in all cases (carbon deposition was not included).

Vermeiren et al. [21] also described the partial oxidation of methane (28.6% CH_4 in air) over 5 wt.-% nickel catalysts and drew similar conclusions to Prettre. They compared the activity for methane partial oxidation with the reported methane steam reforming activity over similar catalysts and found that partial oxidation was 13 times faster than steam reforming. They suggested that the availability of extra reaction pathways (reactions 4–6), substantially accelerate methane conversion in methane/oxygen mixtures.

Huszár et al. [22] have investigated oxygen diffusion during methane oxidation (25% CH_4 in air) in nickel/mullite catalysts at 1033–1273 K. They concluded that the formation of H_2 and CO required the presence of metallic nickel.

Hayakawa and co-workers [23] have synthesised $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide catalysts and have used them for the partial oxidation of methane. Their catalysts showed high activity for synthesis gas production. XRD studies on the used catalysts indicated that nickel oxide segregated from the perovskite structure and was reduced to

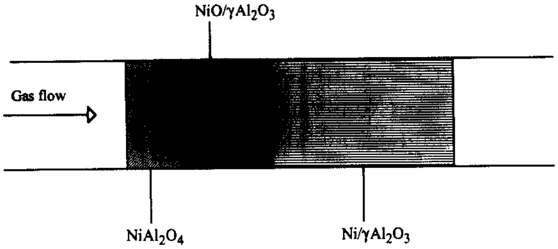

Fig. 3. Schematic of catalyst-bed zones during partial oxidation over 5 wt.-% Ni/Al_2O_3 (after ref. [10]).

nickel metal particles which were thought to be the active catalytic species.

More recently, Lunsford and co-workers [10] using both XRD and XPS methods studied a 25 wt.-% Ni/Al_2O_3 catalyst bed after exposure to the methane partial oxidation reaction. There were three regions in the used catalyst bed (Fig. 3). The first of these contained $NiAl_2O_4$, which has moderate activity for complete combustion of methane to CO_2 and H_2O. The second region was made up of particles of NiO and Al_2O_3, which was thought to complete the total oxidation of methane. The final, third region of the catalyst bed contained supported metallic nickel on alumina. It was suggested that at this stage the thermodynamic equilibrium to synthesis gas was achieved by catalysis of reforming reactions of methane with carbon dioxide and water. Also, XPS studies showed that no surface carbon was formed below 973 K, at which temperature, however, only CO_2 and H_2O were produced. The surface carbon content increased rapidly to a monolayer coincident with the sudden increase in methane conversions at 1023 K. They also showed that the amount of surface carbon generated was primarily influenced by the CH_4/O_2 ratio. At CH_4/O_2 ratios ≥ 2, the reaction produced large amounts of carbon while using CH_4/O_2 ratios ≤ 1.25, no significant surface carbon was formed. However, at this ratio, CO_2 and H_2O were the principal products.

Choudhary et al. [12–14] have recently described a series of catalysts NiO/MO_x (M = lanthanides, Ca, Al, Mg with Ni:M $\geq$ 1:1). They found that carbon deposition during the partial oxidation of methane was very substantial but had little or no influence on catalytic activity and selectivity.

The cobalt-containing perovskite, $Ca_{0.8}Sr_{0.2}Ti_{0.8}Co_{0.2}O_{3-\delta}$ has been tested for methane oxidation ($CH_4/O_2/N_2 = 2.36:1:4$) at 1028 K, both before and after pre-treatment with methane [23]. Before methane pre-treatment the catalyst gave 30.6% methane conversion and 16.9% selectivity to C_2 but no synthesis gas. After methane pre-treatment for an hour at 1048 K, the catalysts became very selective for synthesis gas production, giving 70.9% methane conversion and more than 94% selectivity to CO and H_2. XRD studies revealed new peaks assigned to bulk cobalt metal and $CaTiO_3$. They suggested that the methane pre-treatment caused reduction of $Ca_{0.8}Sr_{0.2}Ti_{0.8}Co_{0.2}O_{3-\delta}$ to give Co metal particles supported on the perovskite and these were responsible for synthesis gas production.

The iron-containing perovskite $Ca_{0.6}\,Sr_{0.4}\,Ti_{0.6}\,Fe_{0.4}\,O_{3-\delta}$ has also been investigated as a methane partial oxidation catalyst [23]. Initially, a substantial amount of synthesis gas was produced, after methane pre-treatment, but the activity was quickly lost, no explanation was given.

Alqahtany et al. [24] have demonstrated synthesis gas production from methane over an iron electrode in an yttria-stabilised zirconia reactor, they found that the reduced iron was more active than oxidised iron for synthesis gas formation. However, carbon deposition occurred on the iron electrode.

3.2. *Noble metal (Pd, Rh, Ru, Pt, Ir) catalysts*

Green and co-workers have examined transition metal catalysts for partial oxidation of methane. A series of rare-earth ruthenium pyrochlores, $Ln_2Ru_2O_7$ were tested for methane oxidation. The catalysts converted methane to synthesis gas with yields and selectivities to synthesis gas closely approaching those expected from thermodynamic calculations, as shown in Fig. 1. Examination of the catalyst after reaction showed reduction had occurred giving ruthenium metal particles on the surface of a defect fluorite $(Ln,Ru)O_{2-x}$. They later showed that Ni, Ru, Rh, Pd, Pt and Ir, either supported on alumina, or present in a mixed oxide precursor also catalysed partial oxidation and dry reforming: however, with the nickel and palladium catalysts substantial carbon deposition was observed. No macroscopic carbon deposition or catalyst deactivation was observed for the iridium and rhodium catalysts [8,9].

Jones et al. have examined europium iridate ($Eu_2Ir_2O_7$) catalysts using in-situ X-ray diffraction and mass spectrometry [25]. This showed the pyrochlore structure of the iridate was destroyed during the initiation of catalysis, giving an active catalyst that was shown to comprise particles of iridium metal of about 30 Å in diameter supported on europium oxide. The sudden increase in synthesis gas production, monitored by mass spectrometry, corresponded to the onset of reduction of pyrochlore. Ashcroft et al. [26] reached similar conclusions in a study of the rare-earth iridium pyrochlore catalysts using in-situ energy dispersive X-ray diffraction by synchrotron radiation.

Kunimori and his co-workers [27] found that $RhVO_4/SiO_2$ and unpromoted Rh/SiO_2 are excellent partial oxidation catalysts giving greater than 90% methane conversion to synthesis gas at around 973 K. They have also compared the activity of the two catalysts at temperatures between 573 K and 993 K at atmospheric pressure, and a CH_4/O_2 ratio of 2 with nitrogen dilution. It was found that, for $RhVO_4/SiO_2$, the onset of activity occurred around 773 K, whilst the unpromoted Rh/SiO_2 catalyst showed the onset of activity at the higher temperatures (above 873 K). Investigation of the used catalysts showed that the average rhodium particle size for $RhVO_4/SiO_2$ was smaller than the rhodium particles in the unpromoted Rh/SiO_2. The difference in activity at low temperature was ascribed to the importance of metal particle size, morphology and its interaction with the oxide support.

The activity towards partial oxidation of methane of catalysts composed of 1 wt.-% palladium supported on a range of oxides has been studied. The reaction was carried out at 1023 K, using a GHSV of 5000 h^{-1} and CH_4/O_2 ratio of 8:1 [28]. The supports included oxides of metals of groups IIIa and IVa, rare-earth oxides, γ-Al_2O_3 and SiO_2. Methane conversions varied from 33.4% to 66.9% but surprisingly they all gave more than 99% selectivity to CO. No data for hydrogen selectivity were given. However, the methane conversions in all cases exceeded the theoretical maximum (25%) for synthesis gas production under their fixed methane and oxygen ratio. In addition, their space velocity of 5000 h^{-1} GHSV is very small compared with those of other researchers. It is thus probable that carbon deposition over the palladium catalysts is responsible for the difference in methane conversions.

A detailed comparison of supported ruthenium and nickel catalysts at 1073 K with $CH_4/O_2/He$ ratios of 8/4/3 and at extremely fast flow-rates (0.893 mol CH_4 kg^{-1} s^{-1}) has been reported [29]. In all cases the product gas compositions deviated from equilibrium values, indicating kinetic control of the products. Interestingly, they found that a ruthenium catalyst with as little as 0.015 wt.-% Ru loading on Al_2O_3 gave higher activity and selectivity than 5 wt.-% Ni on SiO_2. We note that the relative metal activity for steam reforming is $Ru \approx Rh > Ni > Ir > Pd \approx Pt \gg Co \approx Fe$ [30]. The activity order for methane reforming with carbon dioxide was also found to be Ru > Rh, Ni, Ir > Pt > Pd [31]. The similarity between the orders of activity of the metals for partial oxidation of methane, steam reforming and dry reforming of methane is apparent.

Recently, Hochmuth [32] has investigated partial oxidation of methane over Pt–Pd impregnated monolith catalyst under fast reactant flow in pilot plant experiments. He analysed the axial gas compositions and temperature profiles along the catalyst bed and concluded that there was initial exothermic combustion on the front catalyst bed which generated steam, carbon monoxide and carbon dioxide but little production of hydrogen. Then this was followed by steam and dry reforming together with the water–gas shift reaction. The precious metal based catalyst is extremely active driving both reforming reactions to equilibrium very quickly, although, equilibrium was not reached with regard to the water–gas shift reaction.

Hickman et al. [33–37] investigated rhodium and platinum impregnated foam monoliths as catalysts for the partial oxidation of methane. The reactions were carried out using extremely short residence times of between 10^{-4} and 10^{-2} seconds, under adiabatic conditions. Very high selectivities to synthesis gas ($>90\%$) were observed and almost complete conversion of methane could be achieved. They pointed out that the partial oxidation of methane has a residence time advantage over conventional steam reforming, which has residence times of the order of a few seconds (this being due to heat transfer limitations). This means the size of plant could be greatly reduced.

3.3. *Miscellaneous catalysts*

Otsuka et al. [38] have shown that cerium oxide is able to convert methane to synthesis gas with a 2/1 ratio of H_2/CO at 873–1073 K. They demonstrated that the redox properties of cerium oxide allows the direct formation of synthesis gas from methane (reaction 12) and the partially reduced cerium oxide can be reoxidised by CO_2 giving CO as the sole product (reaction 13). They also showed that addition of platinum black into cerium oxide will accelerate synthesis gas formation. However, the H_2/CO ratios became greater than 2 if their catalyst reduction time was longer than 60 min. This implies that carbon deposition occurs during the later stages of reduction.

$$CeO_2 + nCH_4 = CeO_{2-n} + nCO + 2nH_2 \qquad (12)$$

$$CeO_{2-n} + nCO_2 = CeO_2 + nCO \qquad (13)$$

4. Comments on carbon deposition

Many metal catalysts have been shown to achieve conversion of methane and oxygen to equilibrium gas compositions at high temperatures and at industrially applicable residence times, but the calculated gas compositions neglect consideration of the thermodynamically feasible carbon deposition reactions, (reactions 10 and 11). Claridge et al. [39] have systematically investigated carbon deposition on some metal catalysts during the partial oxidation of methane to synthesis gas. It was found that the relative rate of carbon deposition follows the order of $Ni > Pd \gg Rh, Ru, Pt, Ir$. Very little carbon deposition was found over the noble metal catalysts especially those of platinum and iridium for which, even after 200 hours, negligible carbon deposition and no deactivation was observed. This observation agrees with earlier work on catalysts for ethane steam reforming, which showed less carbon formation over noble metal catalysts. It also demonstrates that the causes of macroscopic carbon deposition are independent of the mechanism for synthesis gas production and that carbon deposition can be kinetically avoided by using suitable catalysts.

Electron micrograph studies of used nickel catalysts with a high loading show clearly both ‘whisker’ and ‘encapsulate’ carbon (Fig. 4). These two forms of carbon have also been observed on steam reforming catalysts, in particular for nickel, iron, and cobalt catalysts [3,40]. Whisker carbon deposition does not alter the rate of synthesis gas production, which may explain why no deactivation was reported using similar catalysts for the partial oxidation of methane [10,14,28]. Recently, Rostrup-Nielsen and Bak Hansen [31] also found no whisker carbon on their noble metal catalysts used for dry reforming.

5. Concerning the mechanism of catalytic partial oxidation

The two mechanisms proposed to account for the catalytic conversion of methane and oxygen to synthesis gas may be designated as the ‘combustion and reforming reactions mechanism’, CRR, and ‘direct partial oxidation mechanism’, DPO.

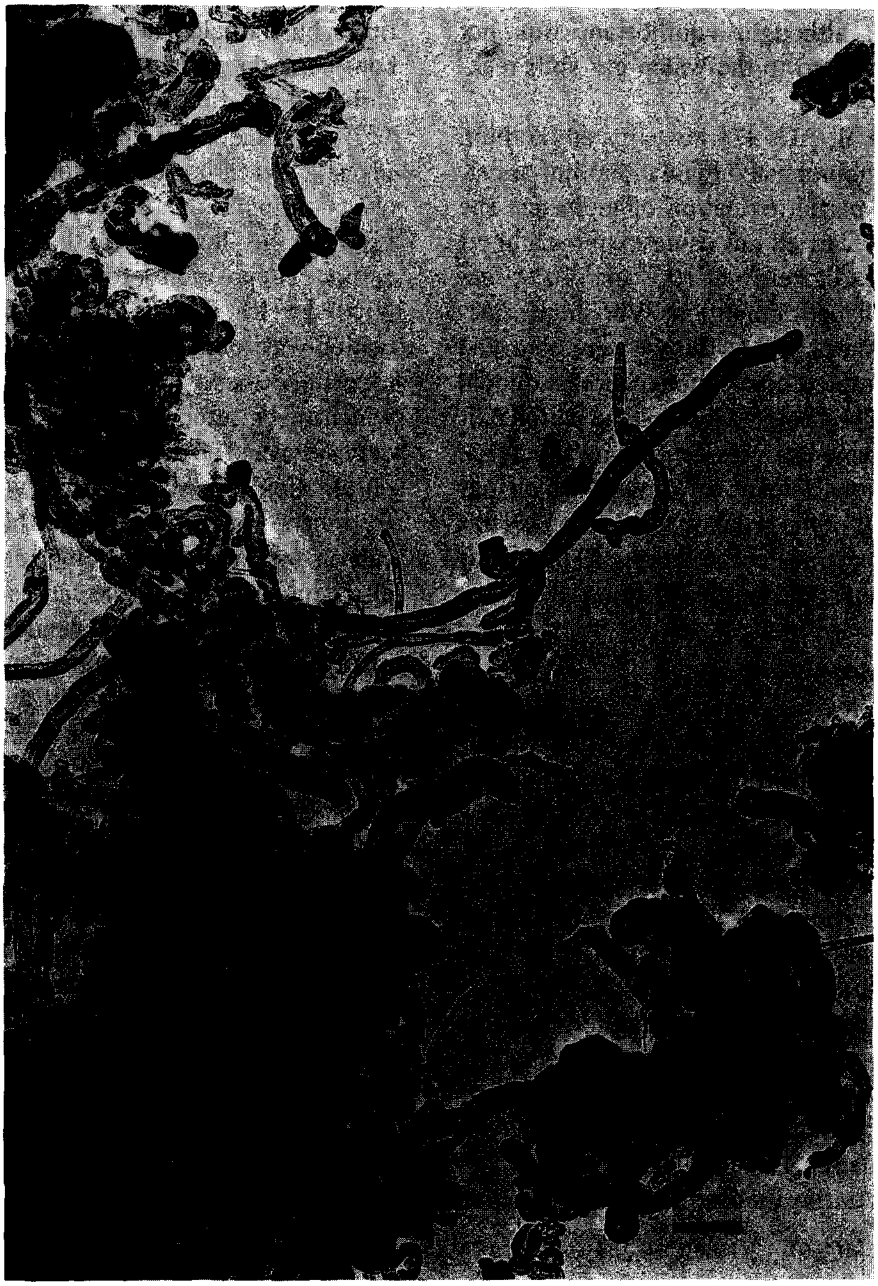

Fig. 4. Micrograph showing the different forms of carbon deposited on the surface of the nickel catalyst. (A) Whisker carbon; (B) encapsulate carbon. The scale bar is 50 nm.

5.1. Combustion and reforming reactions mechanism, CRR

The CRR mechanism was first proposed by Prettre et al. [6], after it was observed that the temperature at the front of the catalyst bed was much higher than the furnace temperature, and this was followed by a temperature drop in the inner part of catalyst bed (Fig. 5). This phenomenon has also been observed by other researchers [10,21]. This temperature profile reflects the occurrence of initial exothermic combustion reactions (reactions 4–6) to give carbon oxides and

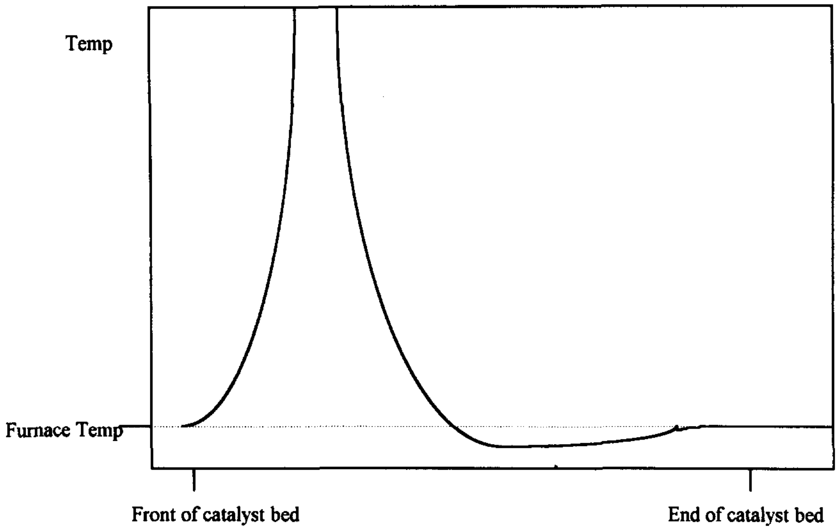

Fig. 5. Schematic representation of the temperature found in partial oxidation catalyst beds (e.g. refs. [6,10], etc.).

water which is followed by endothermic reforming (reactions 7,8) and water–gas shift reactions (reaction 9) to give the synthesis gas. CO and H_2 are the secondary products in this mechanistic scheme. The consequences of changes of space velocity [9,10] and oxygen/methane ratio [9,17] show that selectivities to CO_2 and H_2O increase at the expense of CO and H_2 at larger space velocities or higher oxygen/methane ratios. The group VIII metals have been independently shown to achieve complete combustion [41], and drive carbon dioxide reforming reactions [42,43], steam reforming reactions and water–gas shift reactions to equilibrium [3]. All these observations support CRR mechanisms.

5.2. The direct partial oxidation mechanism, DPO

Recently, Hickman and Schmidt claimed that CO and H_2 are the primary products of the methane partial oxidation reaction [34,36,37] over metal coated monolith catalysts under adiabatic conditions at very short residence times. They observed a substantially higher selectivity to H_2 over Rh compared to that for Pt (86 and 60%, respectively) whereas selectivities to CO were similar for both metals (92 and 95%, respectively). The catalyst-bed exit temperature in the case of Rh was found to be lower than with Pt, suggesting that the Rh surface is more selective for direct synthesis gas formation than Pt (complete oxidation to CO_2 and H_2O generates more heat). Interestingly, they also found no significant improvement in conversion and selectivity as they doubled the residence times. Replacing the monolith catalyst with layers of Pt–10% Rh gauze (further decreasing the residence time) showed that the methane conversion and synthesis gas selectivity over these materials increased with increasing flow-rates, which contradicts previous

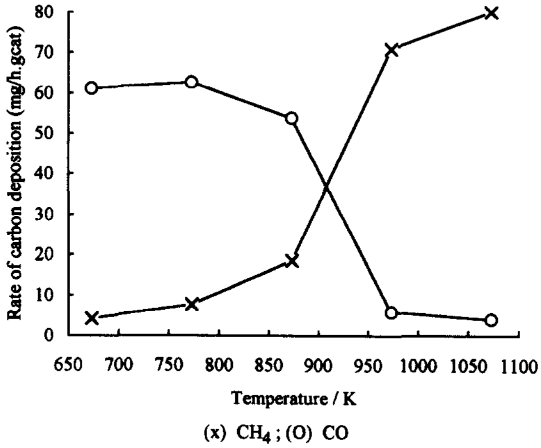

Fig. 6. The effect of temperature on the amount of carbon deposited from pure methane and pure carbon monoxide. Catalyst amount = 50 mg, flow-rate = 8 ml min^{-1}, for 10 min.

observations [9,21]. At a fixed flow-rate, no change in selectivity and conversion was observed as the number of layers of gauze increased, provided that there were at least three layers present. In addition, the product distributions were far from water–gas shift or reforming equilibrium and H_2/CO ratios are lower than predicted at equilibrium. All of these observations cannot be explained by the CRR mechanism. They postulated a sequence of surface reactions for direct formation of synthesis gas, described here as DPO mechanism.

$$CH_4 = C + 4H \qquad (14)$$

$$O_2 = 2O \qquad (15)$$

$$2H = H_2 \qquad (16)$$

$$C + O = CO \qquad (17)$$

$$O + H = OH \qquad (18)$$

$$OH + H = H_2O \qquad (19)$$

$$CO + O = CO_2 \qquad (20)$$

The difference in H_2 selectivity between Pt and Rh was explained by the relatively high activation energy for reaction (18) on a Rh surface [34,37]. The selectivity to CO and H_2 should be optimised at short residence times against subsequent further oxidation. They then developed a model with a 19-step surface mechanism, including those crucial reactions above and found that the product selectivities observed under different reaction conditions could be predicted.

It should be noted that both CRR and DPO mechanisms could be correctly describing the predominant reaction path, depending on the reaction regimes. Hickman and Schmidt conducted their experiments under very different conditions to other researchers. Their residence times are about 10 to 100 times shorter than in other work. Also, the adiabatic conditions cause the catalyst-bed temperature to vary, usually > 1300 K compared with isothermal temperatures of ca. 1000 K and at slightly elevated pressure (1.4 atm). Under these conditions, especially at such short residence times, equilibria for the relatively slow total oxidation and slow reforming would be unlikely to be achieved, thus selective desorption of CO and H_2 from the surface could lead to production of CO and H_2. This DPO route to synthesis gas formation has the advantage of giving a higher productivity of H_2 and CO. Unfortunately, it gives poorer CO and H_2 selectivities compared with those achieved under the CRR mechanism, even at the higher operating temperatures. In addition, the influence of non-catalytic, gas phase synthesis gas production over the monolith at high reaction temperatures has not been studied.

5.3. Reaction routes for carbon formation

The Boudouard (reaction 10) and methane decomposition (reaction 11) reactions are both thermodynamically favourable. Claridge et al. [39] have investigated the rates of carbon deposited from pure CH_4 and pure CO over a supported nickel catalyst at various temperatures. The results are shown in Fig. 6. They show that both reactions are catalysed but to varying extents depending on the operating temperature. At the typical methane partial oxidation temperature of 1050 K, the amount of carbon from pure CO via the Boudouard reaction is very low compared with the amount from the methane decomposition reaction (20 times less) and methane/oxygen reaction (5 times less). This indicates that catalytic methane decomposition is the principal route for carbon formation. Supporting evidence arises from the observation that the carbon build up occurs at the front of the catalyst bed where the methane partial pressure is highest.

Carbon formation from reactions of hydrocarbons and CO over metal particles has been investigated [44]. Commonly for nickel and palladium based catalysts, the carbon grows as a fibre with a metal crystal at the end (whisker). It has been suggested chemisorbed carbon has a high solubility in the metal lattice. Adsorbed carbon atoms that do not react with gaseous molecules diffuse into the metal crystal and nucleate at an unexposed crystal face. Kinetic approaches to preventing carbon formation, including passivating the metal surface with other chemical species to alter its adsorptivity or solubility have been reported for steam and dry reforming [45,46].

6. Methane reforming reaction with carbon dioxide (dry reforming)

This reaction (reaction 3) was first studied by Fischer and Tropsch over a number of base metal catalysts [47]. Calculations indicate that the reaction is thermodynamically favoured above 913 K. It is more endothermic than steam reforming (reaction 1). Carbon deposition is predicted [48], and carbon formation over metal catalysts during the carbon dioxide reforming reaction has been observed [43,46]. An industrial process, the Calcor process, has been developed, which uses methane and a large excess of CO_2 to make CO rich synthesis gas, a nickel based catalyst is indicated [49,50].

Ferrous metals Fe [51], Co [52], Ni [53–55], and noble metals [56–58,42] have all been reported to be active for dry reforming. Iridium supported on Al_2O_3 is also active and no carbon deposition was observed [43]. This Ir catalyst is active for the exothermic partial oxidation of methane and endothermic carbon dioxide reforming and thus both reactions can be carried out simultaneously. This introduces the possibility of fine tuning the thermodynamics using a CH_4, CO_2 and O_2 feedstock.

Perera et al. [58] have also shown that Eu_2O_3 doped with either Ir or Ru, are effective in producing synthesis gas and there is no significant coke formation. X-ray absorption spectroscopy studies indicated the presence of reduced metal on the spent Ru/Eu_2O_3 catalysts. Richardson and Paripatyadar [56] have also shown that Rh supported on alumina catalysed dry reforming at low ratios of CO_2/CH_4 in the temperature range of 873–1073 K with no coke formation. The kinetic avoidance of carbon formation over noble metals has been attributed to high intrinsic reforming rates combined with low carbon formation rates over the metal surfaces, and this can also be achieved by sulphur passivated nickel [31].

Rostrup-Nielsen and Bak Hansen have shown the order of reactivity for dry reforming to be $Ru > Rh > Ni \approx Ir > Pt > Pd$. This is similar to the proposed order for steam reforming, but the superiority of rhodium and ruthenium is less pronounced. It was found that the replacement of steam by carbon dioxide over noble metal catalysts gave similar activation energies, indicating a very similar mechanism of the two cases [31].

An interesting new catalyst for dry reforming reaction has been described by Krylov and his coworkers [59]. They showed that a mixed oxide catalyst, 5 wt.-% Ca–12 wt.-% MnO on Al_2O_3 gave high yield of synthesis gas from methane and carbon dioxide. No deactivation and no carbon deposition were claimed at 1200 K. They postulated a reaction scheme involving gas–solid and solid–solid reactions to produce synthesis gas however, their catalyst appears to have lower activity and equilibrium was not achieved even at the higher temperatures.

7. The future

Catalytic methane partial oxidation and carbon dioxide reforming reactions without carbon deposition have been demonstrated on laboratory and pilot plant scales [32,60]. Patents based on these two processes have been issued regularly [61–66].

Recently Korchnak and Dunster [67] have reported significant economic incentives for methanol plants based on catalytic partial oxidation of natural gas. The replacement of the steam reforming reaction by catalytic methane partial oxidation to generate synthesis gas for further conversion in low pressure downstream processes, e.g. hydroformylation and the Fischer–Tropsch process have been proposed [68,69]. At the present stage, these two alternative processes appear to be promising. However, there remains much work to be done, including studies on carbon deposition at elevated pressures, detailed process engineering studies and process economic assessments, to develop these alternative synthesis gas routes to the level of industrial processes. It should be noted that conventional reactor tubes (containing Cr, Fe, Ni), may catalyse carbon formation. Inert linings may therefore be necessary for carbon-free operation.

Finally, applications of these alternative processes to other areas have been suggested. Small scale production of hydrogen by methane partial oxidation may have advantages over conventional steam reforming processes [29]. An effective way of converting natural gas to both energy and useful chemicals, i.e. synthesis gas from methane partial oxidation using new fuel cell technology has been suggested [70].

The highly endothermic reaction of methane reforming with carbon dioxide may be used in chemical energy transmitted systems suitable for energy transmission. The conversion of solar energy by the chemical heat pipe [56,71] and the effective use of nuclear energy [72] based on this reaction are under consideration. Finally, this reforming reaction removes methane and carbon dioxide, the two important green house gases, and so may arouse some environmental interest.

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