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A study of carbon deposition on catalysts during the partial oxidation of methane to synthesis gas

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The deposition of carbon on catalysts during the partial oxidation of methane to synthesis gas has been investigated and it has been found that the relative rate of carbon deposition follows the order Ni > Pd > Rh > Ir. Methane decomposition was found to be the principal route for carbon formation over a supported nickel catalyst, and electron micrographs showed that both "whisker" and "encapsulate" forms of carbon are present on the catalyst. Negligible carbon deposition occurred on iridium catalysts, even after 200 h.

Keywords: Methane partial oxidation; carbon deposition; kinetic barrier

1. Introduction

We have reported that the rare-earth ruthenium or iridium pyrochlores and other supported group VIII transition metals [1,2] are excellent catalysts for the partial oxidation of methane to synthesis gas. The synthesis gas yield can be greater than 90% when the CH_4/O_2 ratio is near to 2, and this yield corresponds to that predicted for the thermodynamic equilibrium under our experimental conditions provided that carbon deposition does not occur. The reaction of methane and carbon dioxide giving high synthesis gas yields has also been reported over the same types of catalyst [3].

There are two possible mechanisms for carbon formation, these being via the Boudouard reaction (eq. (1)) or the catalytic methane decomposition reaction (eq. (2)):

$$2CO \rightarrow C_{(s)} + CO_2\,, \tag{1}$$

$$CH_4 \rightarrow C_{(s)} + 2H_2,\,. \tag{2}$$

Typical practical performance of the partial oxidation at 1050 K (in the absence of diluent) are methane conversion of 90%, with 98% selectivity to hydrogen, and

95% selectivity to carbon monoxide. At one atmosphere, this corresponds to outlet pressures of: 0.307 atm CO; 0.016 atm CO_2; 0.036 atm CH_4 and 0.628 atm H_2. Thus, the equilibrium constant for the two carbon forming reactions can be calculated:

$$\text{Boudouard reaction}: \quad p(CO_2)/[p(CO)^2] = 0.170\ \text{atm}^{-1};$$

$$\text{methane decomposition}: \quad [p(H_2)^2]/p(CH_4) = 11.0\ \text{atm}.$$

The equilibrium constants for both reactions [4] lie substantially above these values at 0.212 atm^{-1} and 17.1 atm, respectively. In other words, neither equilibria for carbon formation are achieved, and are being driven thermodynamically to the right, i.e. towards carbon formation. In addition, recently, Lunsford and coworkers [5], Vermeiren et al. [6] and Choudhary et al. [7] have independently demonstrated that nickel catalysts are very effective for the partial oxidation of methane, however, they have not addressed the question of carbon deposition. Here we describe a study of carbon deposition for a range of catalysts under conditions for effective partial oxidation of methane to synthesis gas. Further experiments have also been conducted to determine the origin of the deposited carbon and the types of carbon deposited.

2. Experimental

Catalyst samples were heated at the required temperature (usually 1050 K) under an appropriate gas mixture, at a known flow rate for a measured period of time. The gas feedstocks used were methane : oxygen in the ratio 2 : 1, pure methane and pure carbon monoxide.

The catalyst samples were then investigated for deposited carbon by heating them under 30 ml min^{-1} of oxygen whilst the temperature was ramped at a known rate up to 1120 K in a temperature programmed oxidation (TPO) experiment. A Eurotherm 815P was used to monitor and control the temperature, and the exit gas stream was passed to a HP 5971A mass selective detector (MSD) operating in continuous mode. As deposited carbon was burnt off the sample, the resulting carbon dioxide and, in a few cases, carbon monoxide were detected. The response of the MSD to carbon dioxide was established by monitoring the decomposition of weighted amounts of calcium carbonate. The response to carbon monoxide was then determined by reference to carbon dioxide by successively filling the sample loop with the two gases. Various feedstock gases were used in an attempt to establish the source of the carbon.

High resolution analytical electron microscopy was performed using a Jeol 2000FX instrument, on used nickel catalyst samples so that the morphology of the deposited carbon could be determined.

3. Results

The data in table 1 show that a number of supported group VIII transition metal catalysts are active for the partial oxidation of methane giving a synthesis gas yield above 90%, and that the product yields closely approach those predicted by thermodynamic equilibrium calculations [2], which discounts carbon formation. The yields using the rare-earth pyrochlore, $Eu_2Ir_2O_7$ are similar, and it is found under the reducing reaction conditions iridium metal particles are formed to give a supported transition metal catalyst [1], with a high loading of iridium (52%).

Table 2 reports the rate of carbon deposition under the stated conditions on a variety of catalysts as measured by TPO after 24 h reaction. The nickel catalysts were removed after considerably less time, since substantial carbon deposition was already apparent. In a blank reaction it was found that no carbon was deposited on pure alumina powder, or on the walls of the silica reaction tube. Therefore, we deduce that the carbon deposited on the metal loaded catalysts is formed on the metal alone. The data in table 2 show the magnitude of carbon deposition over the group VIII metals to be Ni (>20 mg h^{-1}carbon) $>$ Pd (7.5 mg h^{-1}carbon) $>>$ other transition metals (<0.06 mg h^{-1} carbon). No deposited carbon was detected on the iridium and platinum catalysts after 24 h of reaction, and even in the case of the pyrochlore catalyst, with the high iridium content, no carbon was detected after the same period. Subsequently, the iridium and ruthenium catalysts were chosen for evaluation over a 200 h period and, again it was found that no carbon was observed, at our detection limited, for iridium and only a trace of carbon (<0.02 mg) was found for the ruthenium catalyst.

The above experiments show that a significant amount of carbon can be deposited on palladium and nickel catalysts within a very short time. A commercial nickel Harshaw catalyst (58% Ni/SiO_2 doped with calcium) was used to investigate the rate of carbon deposition as the partial oxidation reaction proceeded. The reaction conditions used were the same as in the previous experiments and the catalyst

Table 1
Results for the methane partial oxidation reaction over a number of catalysts. $CH_4 : O_2 : N_2 = 2 : 1 : 4$, GHSV $= 4 \times 10^4$ h^{-1}, 1050 K, 1 atm

Catalyst	CH_4 conversion (%)	CO selectivity (%)	H_2 selectivity (%)
1% Ru/Al_2O_3	94	97	99
1% Rh/Al_2O_3	94	97	99
1% Pd/Al_2O_3	93	96	98
1% Ir/Al_2O_3	94	97	98
1% Pt/Al_2O_3	94	96	99
Ni/Al_2O_3 [a]	94	97	99
$Eu_2Ir_2O_7$	94	96	98
thermodynamic equilibrium	94	97	98

[a] CRG "F" catalyst from British Gas.

Table 2
Comparison of various catalysts for carbon deposition during the partial oxidation of methane to synthesis gas. Catalyst amount = 50 mg, temperature = 1050 K, $CH_4/O_2 = 2$, flow rate = 8 ml min^{-1}. Time = 24 h

Catalyst	Rate of formation of carbon (mg h^{-1})
1% Ir/Al_2O_3	0.00
1% Rh/Al_2O_3	0.03
1% Pt/Al_2O_3	0.00
1% Ru/Al_2O_3	0.02
5% Rh/Al_2O_3	0.06
5% Ru/Al_2O_3	0.01
5% Pd/Al_2O_3	7.48
$Eu_2Ir_2O_7$	0.00
$Eu_2Ru_2O_7$	0.02
CRG "F" [a]	20.32
CRG "H" [a]	25.58
Ni Harshaw [a]	21.58

[a] The British Gas CRG "F" and CRG "H" nickel catalysts and the nickel Harshaw catalyst were left on stream for 150 min, 80 min and 60 min respectively.

samples were exposed to the reaction for periods of 5 min to 1 h. The results are shown in fig. 1. It can be seen that the total amount of carbon deposited increased with time but that the rate of this carbon deposition decreased rapidly. After 1 h problems were caused by the occurrence of a reduction in gas flow rate, presumably due to large amounts of deposited carbon blocking channels between the catalyst

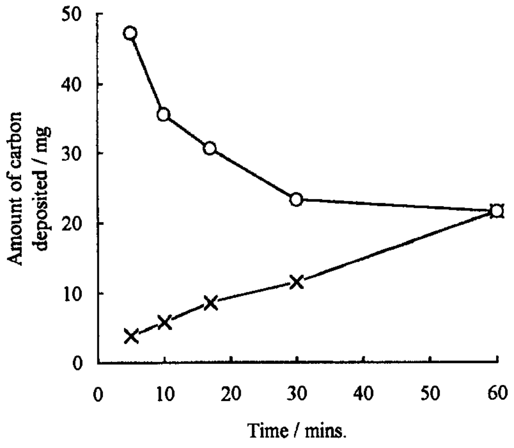

Fig. 1. Rate of carbon formation over the nickel Harshaw catalyst. Catalyst amount = 50 mg, temperature = 1050 K, $CH_4/O_2 = 2$, flow rate = 8 ml min^{-1}. (×) Total amount of C deposited (mg), (○) rate of C deposition (mg h^{-1}).

powder. Indeed, more than 20 mg of carbon was found on the 50 mg of catalyst after 1 h. Electron microscopy showed that substantial carbon deposition had occurred after only 5 min.

The electron micrograph (under magnification of 140,000) in fig. 2 shows the presence on the nickel catalyst of tubular carbon filaments (whisker carbon) with a co-axial channel. The dark spot at the end of a long filament is a small nickel particle (3–7 nm diameter) with a very similar diameter to the carbon filament tube. Another form of carbon (encapsulate carbon) can also be seen in the micrograph, completely enclosing a larger nickel particle (≈ 60 nm diameter).

In order to determine the source of the deposited carbon over the partial oxidation catalysts, catalyst samples were heated at various temperatures under either CH_4 or CO for 10 min and then TPO experiments were carried out. In the data shown in fig. 3 it is noticeable that at the temperatures used for the partial oxidation reaction, i.e. > 1020 K, only a small amount of carbon is deposited by CO but rela-

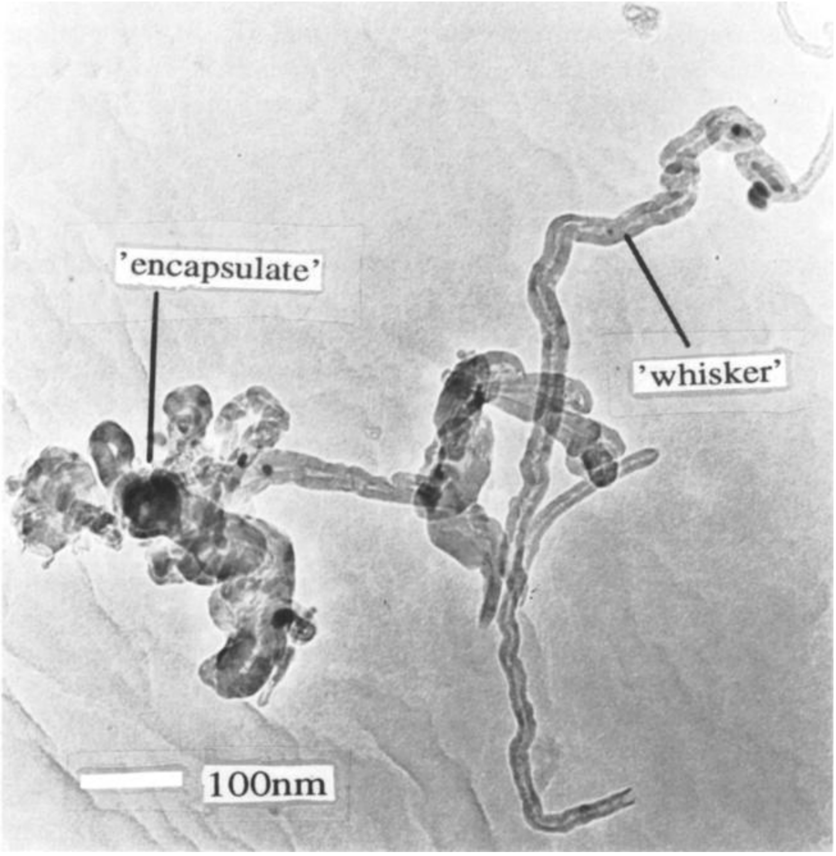

Fig. 2. Micrograph showing the different forms of carbon deposited on the surface of the nickel catalyst.

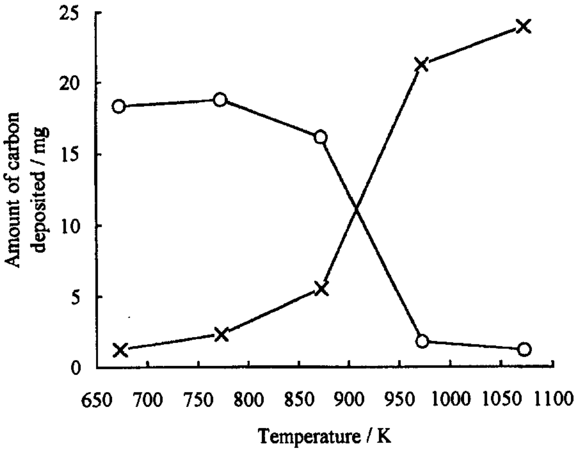

Fig. 3. The effect of temperature on the amount of carbon deposited from pure methane and pure carbon monoxide. Catalyst amount = 50 mg, flow rate = 8 ml min^{-1}, for 10 min. (×) CH_4; (○) CO.

tively large amounts of carbon are deposited from CH_4. At lower temperatures the amount of carbon from each source changes dramatically to give the opposite effect. At 890 K the amount of carbon from each source is essentially equal.

4. Discussion

Carbon deposition on the catalyst during the partial oxidation of methane to synthesis gas is undesirable. It is, therefore, one of the important considerations before this process can be used on an industrial scale. The deposition of carbon from carbon containing gaseous molecules has been extensively studied before. Kinetically, both the Boudouard reaction and the methane decomposition reaction giving undesirable carbon are known to be exceptionally slow in the absence of a catalyst, but both can be readily catalysed by many transition metals. The work of Audier et al. [8] clearly demonstrated that a significant amount of carbon can be deposited over catalysts containing iron or nickel. In order to avoid carbon deposition on the iron containing reactor walls, reactions must, therefore, be carried out in glass or ceramic lined reactors. Although nickel catalysts are reported to be very effective for partial oxidation of methane to synthesis gas, they are unsatisfactory with respect to carbon deposition, as also shown in some conditions of steam reforming process [9]. The rate of deposition of "whisker" type carbon on nickel catalysts is essentially independent of time, and can lead to the accumulation of large amounts of carbon on the catalyst, which it is suggested to cause the break up of the nickel metal particles of the catalyst [4]. The encapsulate form of carbon has been reported to build up with time and to deactivate the catalyst by covering the nickel surface [10]. Extensive HREM studies of graphite whiskers and encapsulate carbon formed over Ni alloys at different temperatures have been reported [8].

Other workers have observed that the Boudouard reaction is 10 times as fast as the decomposition of methane over nickel catalysts under their conditions [11], and this coupled with the fact that the effluent gases from the reactor contain much more carbon monoxide than methane, suggests that the Boudouard reaction will be the principal route to carbon formation. However, we have found that at the higher temperatures investigated, and those used for the partial oxidation reaction, the amount of carbon from the pure carbon monoxide via the Boudouard reaction is very low compared with the amount deposited from the methane decomposition reaction (20 times less) and methane/oxygen reaction (5 times less) at 1050 K at the same residence time. At the lower temperatures, i.e. 670 K, and those temperatures typically used for converting synthesis gas to methane in methanation reaction the most thermodynamically favoured carbon forming reaction is the Boudouard reaction, and this is indeed shown to be the case in our experiments. Further evidence that the methane decomposition reaction is important under the partial oxidation conditions is that the carbon build up occurs at the front of the catalyst bed where the methane partial pressure is highest.

The absence of carbon formation over some of the group VIII metal catalysts is entirely attributed to the kinetic limitation of the carbon formation reactions assisted by high space velocities and inert reactor linings.

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