

New Catalysts for the Conversion of Methane to Synthesis Gas: Molybdenum and Tungsten Carbide

John B. Claridge,¹ Andrew P. E. York, Attila J. Brungs, Carlos Marquez-Alvarez,² Jeremy Sloan,
Shik Chi Tsang,³ and Malcolm L. H. Green⁴

The Catalysis Centre, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, United Kingdom

Received June 12, 1998; revised August 17, 1998; accepted August 18, 1998

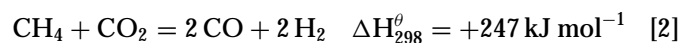
High-surface-area molybdenum and tungsten carbide materials, synthesised by the temperature programming reduction of the relevant metal oxide with methane/hydrogen, are highly efficient catalysts for the conversion of methane to synthesis gas, via the steam reforming, dry reforming, or partial oxidation processes. The activities of the carbides were found to be comparable to those of elemental iridium and ruthenium (well known to be active noble metal catalysts for the reforming of methane), and the conversion and product distribution were in accord with those calculated from the thermodynamic equilibria. At ambient pressure the carbides deactivated, in all the processes, due to the oxidation of the catalyst to MO₂, while operation at elevated pressure (8 bar) resulted in stabilisation of the carbide and no catalyst deactivation for the duration of the experiments (72 h). HRTEM analysis showed that no macroscopic carbon was deposited on the catalysts during the catalytic reactions. The deactivation rate of the carbides reflected the strength of the oxidant used: oxygen > water \cong carbon dioxide. A deactivation mechanism, via the insertion of O* resulting in oxide terraces is discussed, and two possible mechanisms for the production of synthesis gas by the methane dry reforming reaction over metal carbides are proposed: noble metal type and redox type. © 1998 Academic Press

INTRODUCTION

Natural gas, the main component of which is methane, is an abundant fossil fuel resource found all over the world and is predicted to outlast oil reserves by a significant margin (1). Most of these reserves, however, are situated in areas remote from the centres of highest energy consumption (2), and the costs of compression, transportation and storage make methane an unattractive proposition as an energy source (3). To make methane economically more

viable, a large amount of research into the conversion of methane to liquids or higher hydrocarbons has been carried out. For example, the direct oxidative conversions of methane into methanol (4–7), formaldehyde (8, 9), benzene and other aromatics (10, 11), and propanal (12, 13) have all been demonstrated, but unfortunately the yields achieved are too low or the processes too costly. The most promising of the direct conversion routes is the oxidative coupling of methane to ethane and ethene. However, an inherent mechanistically imposed limit to the maximum C₂ yield appears to exist, limiting the maximum yield to about 30% (14, 15); in fact, the highest reported yields in the literature are lower than this, at around 20–25% (16–20), and do not meet industrial requirements at the current price of oil (21).

Current industrial use of methane as a chemical feedstock proceeds by initial conversion to carbon monoxide and hydrogen (synthesis gas) by either steam reforming (22) [1] (the most widespread process) or by dry reforming [2]. In addition, while currently limited as an industrial process, partial oxidation [3] has recently attracted much attention due to significant inherent advantages (e.g., exothermicity). The synthesis gas produced is then used in downstream processes, such as methanol synthesis, Fischer–Tropsch synthesis, or ammonia synthesis.



Nickel catalysts are used commercially for both methane steam and dry reforming reactions (22), while partial oxidation is carried out autothermally (23). However, nickel also catalyses carbon formation, via methane decomposition [4] and CO disproportionation (Boudouard reaction) [5], both of which lead to catalyst deactivation and plugging of the reformer tubes by carbon deposits. Excesses of oxidants are used in order to prevent carbon deposition, but this increases the H₂/CO and/or CO₂/CO ratios; low H₂/CO and CO₂/CO ratios are required for optimal further conversion

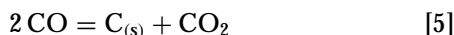
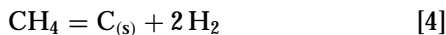
¹ Current address: Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208.

² On leave from Instituto de Catálisis y Petroleoquímica, CSIC, Campus Cantoblanco, 28049 Madrid, Spain.

³ Current address: The Catalysis Research Centre, Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK.

⁴ To whom correspondence should be addressed. E-mail: malcolm.green@chem.ox.ac.uk.

of the synthesis gas to higher hydrocarbons, alcohols, or for iron ore reduction (i.e., reducing gas) (3, 22).



Therefore, considerable effort has been concentrated on exploring catalysts for reactions [1]–[3] which are resistant to carbon formation at or near stoichiometric reactant ratios. Previously sulphur passivated nickel catalysts (24) and noble metal catalysts (25–30) have been shown to exhibit kinetic resistance to carbon formation, but the low activities of sulphur passivated nickel and the high costs and limited availability of the noble metals have limited their application.

Since 1973, when Levy and Boudart reported that α -WC displayed reactivity similar to Pt for *neo*-pentane isomerization (31), there has been considerable interest in the catalytic properties of metal carbides, particularly of the group VI transition metals, for a variety of reactions (32, 33). Indeed, since the starting materials for the production of these carbides are abundant and cheap, it has been suggested that they can replace the rare and expensive noble metals in catalysis. The main problem with the metal carbides has been the difficulty in obtaining materials with sufficiently high surface area for catalytic applications. However, a number of research groups have now published methods for synthesising metal carbides with surface areas as high as 200 m² g⁻¹ (34–41). These carbide materials have shown promise for a number of reactions, including HDN and HDS (42–45), hydrocarbon isomerization (46–52), and CO hydrogenation and Fischer–Tropsch synthesis (53–55).

Here we demonstrate that the carbides of molybdenum and tungsten are extremely active catalysts for the oxidation of methane to synthesis gas with carbon dioxide (dry reforming), oxygen (partial oxidation), or steam (steam reforming), using a stoichiometric feedstock at slightly elevated pressures. These are reactions that are normally catalysed by the noble metals. Also, importantly, no carbon deposition was observed over the carbides during the reactions, and the consequential selectivities and conversions to carbon monoxide and hydrogen are those predicted by thermodynamic considerations.

METHODS

Catalyst Synthesis

The high-surface-area metal carbide materials were prepared by the methods previously described for β -Mo₂C (36), α -WC (56), and Mo₂C/Al₂O₃ (57), by the temperature-programmed reduction (TPR) of the relevant oxides or supported oxides in flowing methane or methane/hydrogen mixture. Briefly, the details of the TPR synthesis are as follows: The precursor material was heated, under

20% v/v CH₄/H₂ or pure CH₄, from room temperature to 1000–1150 K, depending on the material (synthesis of WC requires a higher temperature than for Mo₂C), at a heating rate of 1 K min⁻¹. Normally the catalysts were prepared *in situ* and tested immediately. The 5 wt% Mo₂C/Al₂O₃ was prepared from γ -Al₂O₃ (AKZO, 297 m² g⁻¹ (000-1.5 E, high purity)) impregnated with a solution of (NH₄)₆Mo₇O₂₄ · 4H₂O. The mixture was dried in air at 373 K for 10 h and then ramped at 10 K min⁻¹ to 770 K and held for 15 h, to give the supported carbide precursor.

The postsynthesis high-surface-area carbides or supported carbides are readily and exothermically oxidised by air at room temperature and, therefore, passivation in flowing 1% O₂/N₂ for 10 h at room temperature is required before exposure to the atmosphere and characterization can be achieved (57).

The 5 wt% Ir/Al₂O₃ catalyst was prepared by impregnating 5.00 g of Al₂O₃ (AKZO, high purity; surface area = 297 m² g⁻¹) with a solution containing 0.624 g of (NH₄)₃IrCl₆. The mixture was dried in air at 373 K for 10 h and calcined in air at 770 K for 22 h. The 5 wt% Ru/Al₂O₃ and 5 wt% Rh/Al₂O₃ catalysts were obtained from Johnson-Matthey Ltd.

Catalyst Testing

The apparatus used in this work was a modified version of the commercial Labcon microreactor (see Fig. 1). The reactor was built using 1/8 and 1/16-in.-od 316 stainless steel tubing and 316 stainless steel Swagelok fittings throughout. Gas flow rates were controlled using Brooks 5850TR mass flow controllers, and the gases were then combined and passed to the reactor, either directly or via the mixing valve (MV) when liquid was being supplied. Water flow rates, for steam reforming, were controlled using a Bronkhorst LIQUI-FLOW liquid flow controller, operating with an 8-bar helium over pressure. From here, it passed to the mixing valve, where it was mixed with the gas flow, and then to the Bronkhorst vaporiser. The liquid flow controller and vaporiser were controlled by a Bronkhorst HighTech EPA2 control module. The catalyst sample (generally 0.33 g) was placed between two quartz wool plugs in the centre of a 4-mm-i.d. silica tube and inserted into a vertical Severn Science tube furnace, heated to the required reaction temperature, and controlled from a Eurotherm 905 temperature controller. Calibration of the furnace allowed accurate and reproducible reaction temperatures to be used in the experiments, and no significant cooling or heating effects were observed (endothermic or exothermic reactions). For safety reasons, in the experiments carried out at elevated pressures, the silica tube was placed inside a steel tube and sealed at both ends with rubber O rings to ensure that no gas could pass into the space between the two tubes. The exit gas stream from the reactor passed through a Tescom two-stage

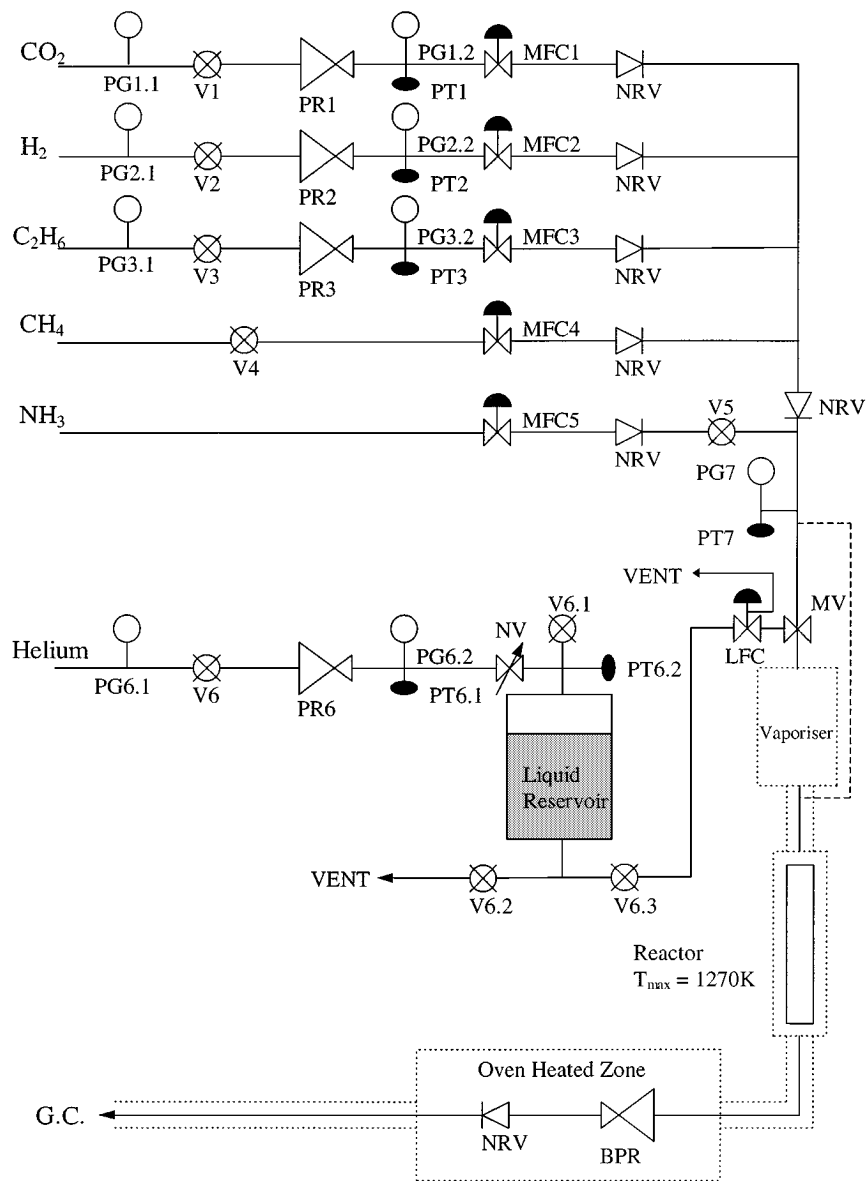


FIG. 1. Schematic diagram of the modified Labcon microreactor (PG, pressure gauge; V, manual On/Off valve; PR, pressure regulator; PT, pressure transducer; MFC, mass flow controller; NRV, non-return valve; MV, mixing valve; NV, needle valve; LFC, liquid flow controller; BPR, back pressure regulator).

back-pressure regulator, which provided a smooth pressure drop across the reactor bed. All the pipework was heated to prevent condensation of the products.

Product analysis was carried out using a Hewlett-Packard 5890II gas chromatograph, fitted with both a thermal conductivity detector and a methanator/flame ionization detector. Separation of the products was achieved using a 3-m Porapak Q packed column, with argon carrier gas. Reference data and pure component injections were used to identify the major peaks, and response factors for the products and reactants were determined and taken into account in the calculation of the conversion and product distribution. In all cases stoichiometric gas mixtures were

used and carbon balances were better than 97%. Calculation of conversions and yields was carried out according to the general equations below:

$$\text{conversion of } x = C[x] = (\% \text{ conversion of } x \text{ into all products}).$$

$$\begin{aligned} \text{yield of carbon monoxide} &= Y[\text{CO}] \\ &= (\text{amount of CO in products}) / \\ &\quad (\text{amount (C) in reactants}). \end{aligned}$$

$$\text{H}_2/\text{CO} = (\text{amount of H}_2 \text{ in products}) / (\text{amount of CO in products}).$$

Catalyst Characterisation

The crystalline components of the materials were identified by X-ray diffraction (XRD) using a Philips PW1710 diffractometer with $\text{CuK}\alpha$ radiation. Samples were mounted on an aluminium plate with a groove cut into it and smoothed flat using a microscope slide.

High-resolution transmission electron microscopy (HRTEM) was carried out using Jeol 2000FX and 4000EX electron microscopes with accelerating voltages of 200 and 400 kV, respectively. Samples were ground to a fine powder and dispersed in AR-grade chloroform. The dispersed sample was then placed in an ultrasonic bath for 10–20 min, before a drop of the suspension was placed on a grid, and the grid positioned in the microscope specimen holder.

Catalyst surface areas were determined using an all-glass high-vacuum line and calculated from the N_2 BET isotherms. Hydrogen chemisorption was performed at room temperature using a silica U tube, in which the carbide materials were prepared or the supported noble metal materials reduced; this was attached to the same apparatus as for BET determination. Hydrogen dosing was then carried out and the number of titrated metal sites calculated.

RESULTS

Catalyst Characterisation

The X-ray diffraction patterns of the starting metal oxides and their carbides, after synthesis under the methane TPR conditions, were obtained. None of the starting orthorhombic MoO_3 or WO_3 could be seen in the patterns for the metal carbides, and only minute traces of MoO_2 were observed in the pattern for the molybdenum sample; this is probably due to slight oxidation on removal of the sample from the reactor; however, the very sharp oxide peaks are a stark contrast to the broad carbide peaks, indicating that only a very small amount of oxide is present. The patterns corresponded to almost phase pure $\beta\text{-Mo}_2\text{C}$ and phase pure $\alpha\text{-WC}$, respectively. No evidence of MoC or W_2C , respectively, was ever observed in the XRD patterns of the bulk carbide samples.

The BET surface areas of the samples used for dry reforming, partial oxidation, and steam reforming were $\beta\text{-Mo}_2\text{C} = 30 \text{ m}^2 \text{ g}^{-1}$ and $\alpha\text{-WC} = 20 \text{ m}^2 \text{ g}^{-1}$. The surface areas of the samples used in the activity study are given in the relevant section.

Methane Dry Reforming

Table 1 shows the results obtained for the dry reforming of methane to synthesis gas with carbon dioxide ($\text{CH}_4/\text{CO}_2 = 1$), using $\beta\text{-Mo}_2\text{C}$ and $\alpha\text{-WC}$ as catalysts, at both ambient pressure and elevated pressure. The results shown for the reaction at ambient pressure are those obtained after about 1 h since, under these conditions, the

TABLE 1

Dry Reforming of Methane over the Metal Carbides at Various Temperatures and Pressures ($\text{GHSV} = 2.87 \times 10^3 \text{ h}^{-1}$, $\text{CH}_4/\text{CO}_2 = 1$)

Catalyst	<i>T</i> (K)	<i>P</i> (bar)	C[CH ₄] (%)	C[CO ₂] (%)	Y[CO] (%)	H ₂ /CO
$\beta\text{-Mo}_2\text{C}$	1120	1.0 ^a	92.4	92.5	92.5	0.93
	1220	1.0 ^a	98.8	95.9	95.9	0.92
	1120	8.3	62.5	75.9	69.5	0.78
	1170	8.3	73.5	83.7	78.8	0.83
	1220	8.3	83.3	89.5	86.5	0.88
$\alpha\text{-WC}$	1120	1.0 ^a	92.0	93.1	92.6	0.94
	1120	8.3	62.7	75.4	68.6	0.79
$\beta\text{-Mo}_2\text{C}/\text{Al}_2\text{O}_3$	1120	1.0 ^a	92.6	92.4	92.5	0.95
	1120	8.3	65.1	80.7	73.1	0.81

^a Catalyst deactivates.

catalyst deactivated after a short period of time on stream (8 h), as can be seen in Fig. 2.

Powder XRD showed that the initial $\beta\text{-Mo}_2\text{C}$ was converted to MoO_2 (Fig. 3a), which has only a very low activity for methane dry reforming. *In situ* XRD experiments (not shown) showed that under a flow of CO/H_2 1/1 the carbide phase was stable, while under CO_2/CH_4 1/1 MoO_2 started to appear after an induction period of several hours. No other phases were observed. Further evidence for the oxidation of the catalyst being responsible for deactivation, and not a symptom of deactivation, comes from the observation that passivated samples showed low initial activities and rapid decreases in activity. Increasing the reaction temperature to 1220 K had little or no effect on the lifetime of the $\beta\text{-Mo}_2\text{C}$, and again there was a sudden decrease in activity after approximately 8 h on stream. In addition, at 1120 K, $\beta\text{-Mo}_2\text{C}$ and MoO_2 can be cycled at low conversions under alternating flows of CO_2 and CH_4 , with products approximately of the composition given in the equations

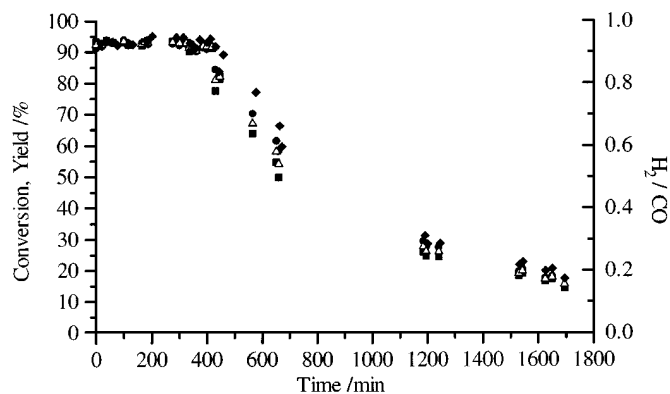


FIG. 2. Lifetime study of $\beta\text{-Mo}_2\text{C}$ for the methane dry reforming reaction at atmospheric pressure and 1120 K ($\text{GHSV} = 2.9 \times 10^3 \text{ h}^{-1}$, $\text{CH}_4/\text{CO}_2 = 1$); ■, C[CH₄]; ●, C[CO₂]; △, Y[CO]; and ◆, H₂/CO.

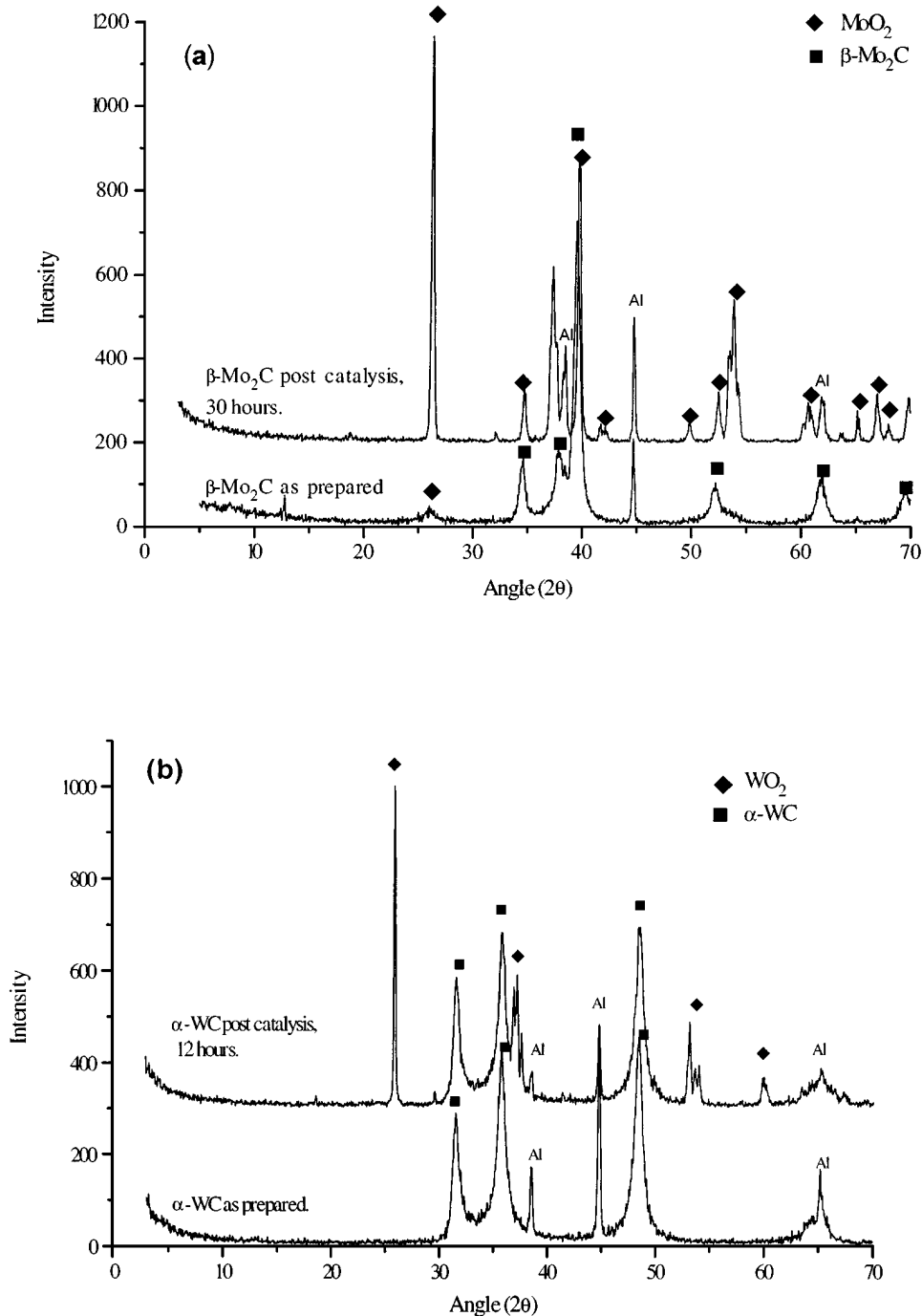
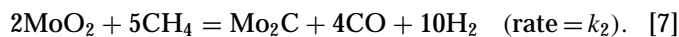
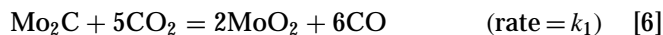


FIG. 3. XRD of (a) $\beta\text{-Mo}_2\text{C}$ and (b) $\alpha\text{-WC}$ before and after methane dry reforming at atmospheric pressure ($T=1120$ K, GHSV = 2.9×10^3 h $^{-1}$, $\text{CH}_4/\text{CO}_2=1$).



This indicates that the early transition metal carbides can function as redox catalysts for the dry reforming of methane.

When the dry reforming reaction was carried out at elevated pressure, the high activity was maintained for the

duration of the experiments, typically more than 72 h (Figs. 4a and 4b), with no observable deterioration in activity. XRD of the quenched catalysts after use (Figs. 5a and 5b) showed only peaks corresponding to $\beta\text{-Mo}_2\text{C}$ and $\alpha\text{-WC}$, respectively, and no trace of MoO_2 or WO_2 was observed. It can also be seen that the peaks for $\beta\text{-Mo}_2\text{C}$ are sharper after the reaction, and this is probably due to some sintering of the catalyst.

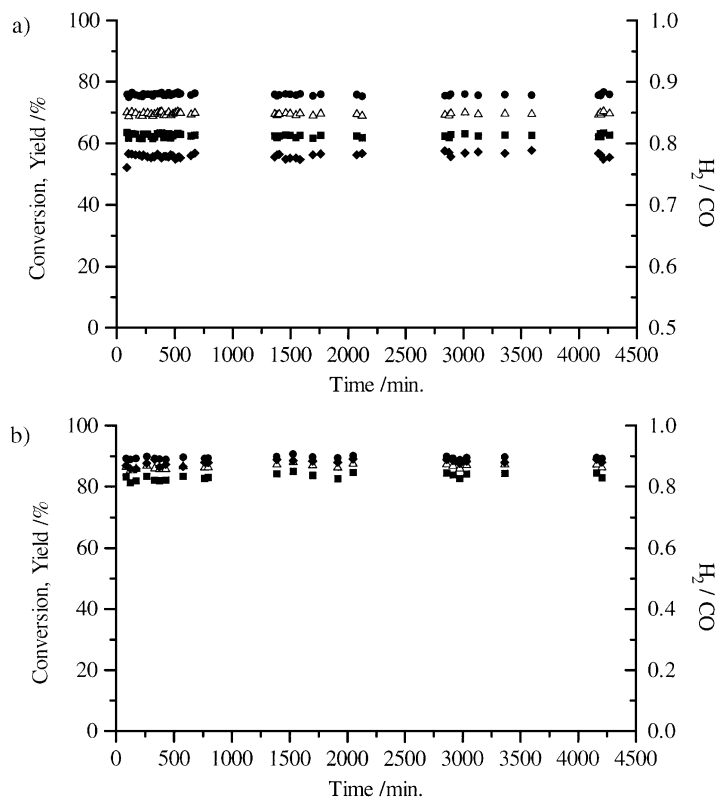


FIG. 4. Lifetime study of β -Mo₂C for the methane dry reforming reaction at 8.3 bar (GHSV = 2.9×10^3 h⁻¹, CH₄/CO₂ = 1). (a) 1120 K and (b) 1220 K; ■, C[CH₄]; ●, C[CO₂]; △, Y[CO]; and ◆, H₂/CO.

Temperature and pressure dependence studies were conducted over a β -Mo₂C catalyst, at temperatures varying from 1120 to 1220 K and at pressures of 1.0 and 8.3 bar. The changes in methane and carbon dioxide conversion and carbon monoxide yield are shown in Table 1. These show the trends expected from thermodynamic considerations (7), with Y[CO], C[CH₄], C[CO₂], and H₂/CO decreasing with increasing pressure and increasing with increasing temperature.

The effect of gas hourly space velocity (GHSV; total gas flow under standard conditions) at 1123 K and 1 bar is shown in Fig. 6. Clearly, as the GHSV is increased the stability of the Mo₂C catalyst diminishes, from >1000 min at 1.91×10^3 h⁻¹ to <1 min at 6.36×10^3 h⁻¹. However, this may simply be due to an increase in the oxidant-to-catalyst ratio. Therefore, an experiment was conducted in which the flow rates of CH₄ and CO₂ were the same as in the experiment above with the lowest GHSV, but the GHSV was increased by the addition of argon (GHSV = 8.79×10^3 h⁻¹). In this case, the oxidant-to-catalyst ratio was the same as in the original experiment, but the catalyst deactivated at a much faster rate. This indicates that GHSV is of vital importance for the stabilisation of the early transition metal carbides under these stoichiometric reactant flows. In addition, it can be seen that the CO₂ conversion is always higher than that of CH₄, indicating that the reaction of CO₂

with the molybdenum carbide (reaction [6], k_1) is more favourable than the reverse reaction of CH₄ and molybdenum oxide (reaction [7], k_2). Indeed, it appears that the rate of divergence of the CH₄ and CO₂ conversions is greater for the experiment with argon, again indicating that $k_1 > k_2$.

In industry it is usual to use supported catalysts, often for reasons of lower costs or improved stability, and, therefore, an alumina-supported molybdenum carbide catalyst (5 wt% β -Mo₂C/Al₂O₃) was tested for the methane dry reforming reaction, and the results are given in Table 1. It can be seen that the supported catalyst showed behaviour similar to that of the unsupported molybdenum carbide. Again the catalyst deactivated at ambient pressure, while the activity was maintained when elevated pressures were employed. This demonstrates that a stable and active molybdenum carbide phase can be formed on an alumina support and that the phase produced is very similar to that formed in the bulk molybdenum carbide sample.

Activity Study

The activity of the group VI transition metal carbide catalysts was investigated for the methane dry reforming reaction, so that a comparison with the noble metal catalysts could be made. As the catalysts are prone to oxidation

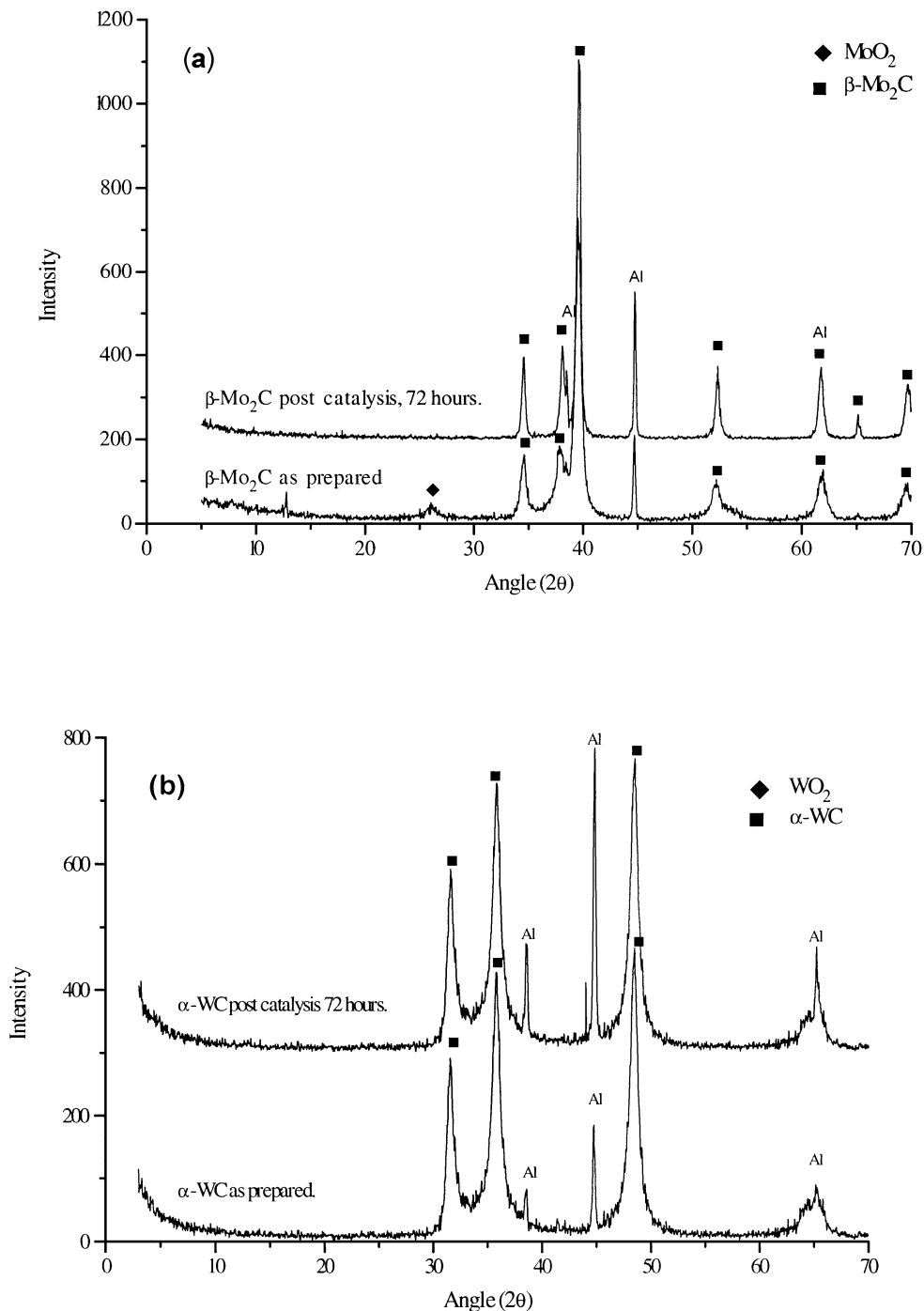


FIG. 5. XRD of (a) $\beta\text{-Mo}_2\text{C}$ and (b) $\alpha\text{-WC}$ before and after methane dry reforming at 8.3 bar ($T = 1120$ K, GHSV = 2.9×10^3 h $^{-1}$, $\text{CH}_4/\text{CO}_2 = 1$).

under the CH_4/CO_2 reaction mixture, the initial activities were measured. Experiments were carried out between 900 and 970 K, so that differential conditions (conversion <10%) could be maintained. Table 2 shows the metal surface site concentration titrated by hydrogen chemisorption at room temperature, and Fig. 7 is a plot of the natural logarithm of the specific activities (mol site $^{-1}$ s $^{-1}$) against

$1000/T$. The 5 wt% Ru/ Al_2O_3 was the most active of all the catalysts tested. However, $\beta\text{-Mo}_2\text{C}$ ($S_g = 91$ m 2 g $^{-1}$) had activity comparable, based on turnover rates, to those of 5 wt% Ir/ Al_2O_3 and 5 wt% Rh/ Al_2O_3 , which are well known as active catalysts for steam reforming and dry reforming (29), while $\alpha\text{-WC}$ ($S_g = 39$ m 2 g $^{-1}$) had a slightly lower activity. From this study and some of the past

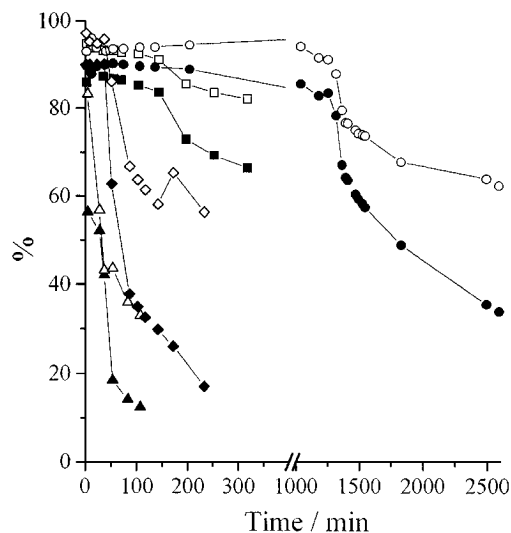


FIG. 6. Effect of GHSV on the stability of the Mo_2C catalyst at 1123 K and 1 bar. Open symbols, $\text{C}[\text{CO}_2]$; closed symbols, $\text{C}[\text{CH}_4]$. GHSV (h^{-1}): \circ , 1.91×10^3 ; \square , 3.97×10^3 ; \triangle , 6.36×10^3 ; \diamond , $[1.91 \times 10^3 + \text{Ar}] = 8.79 \times 10^3$.

literature (25, 58, 59), the relative activities of a number of the dry reforming catalysts have been established as highest $\text{Ru} > \text{Rh} \approx \text{Mo}_2\text{C} > \text{Ir} > \text{WC} > \text{Pd} > \text{Pt}$.

Carbon Formation

Given the propensity for carbon formation, and particularly whisker formation, during the dry reforming of methane (29, 60, 61), the catalysts were studied for carbon deposition postreaction. This was done by HRTEM, as the possible presence of both nonstoichiometric carbides and carbon deposits means that controlled temperature programming oxidation (TPO) results are less informative than in the case of supported metals. An HRTEM study of a postcatalysis β - Mo_2C sample is shown in Fig. 8a. No macroscopic carbon deposition is observed on the catalyst, and the porous morphology of the starting carbide is retained. In contrast, under these stoichiometric conditions large amounts of carbon were deposited over a commercial nickel catalyst, resulting in rapid plugging of the reactor tube. HRTEM examination of the used nickel catalyst

TABLE 2

Kinetic Parameters for the Dry Reforming of Methane over Metal Carbides and Supported Noble Metals ($\text{CH}_4/\text{CO}_2 = 1$, 2 bar, GHSV = $4.4 \times 10^5 \text{ h}^{-1}$)

Catalyst	Chemisorption sites (sites $\text{g}^{-1} \times 10^{19}$)	Rate ($k_{970\text{K}}$) ($\text{mol g}^{-1} \text{ s}^{-1}$)	$E_a \pm 2$ (kJ mol^{-1})
β - Mo_2C	0.22	5.4×10^{-6}	100
α -WC	0.13	1.4×10^{-7}	205
5% Ir/ Al_2O_3	1.31	1.5×10^{-5}	146
5% Rh/ Al_2O_3	7.83	1.4×10^{-4}	46
5% Ru/ Al_2O_3	0.48	4.9×10^{-5}	48

showed the presence of both whisker (W) and encapsulate carbon, as shown in Fig. 8b. Kinetically, both the Boudouard reaction and methane decomposition reaction are slow in the absence of a catalyst, but both are catalysed by many transition metals, and Audier *et al.* demonstrated that a significant amount of carbon can be deposited over catalysts containing iron or nickel (30, 62). In order to avoid carbon deposition on the iron (and sometimes nickel) containing walls of the reactor, reactions have been carried out in a silica-lined reactor. The behaviour of the carbides toward carbon formation appears to be comparable with that of the noble metals tested previously for the methane reforming reactions (29, 30, 63), where it was found that almost no carbon deposition was observed over supported Rh, Ir, Ru, and Re catalysts. This is not surprising since the catalytic similarities between Mo_2C and Ru, and WC and Pt have been reported before (34, 64, 65). It appears that there is a kinetic barrier for carbon deposition over both Mo_2C and WC, as was previously reported for some of the noble metals. Based on the results presented here and those published previously, the relative rate of carbon formation over the catalysts is $\text{Ni} > \text{Pd} \gg \text{Rh}, \text{Ir}, \text{Ru}, \text{Re}, \text{Mo}_2\text{C}, \text{WC} \approx 0$.

Methane Partial Oxidation

Since the metal carbides were found to be highly active catalysts for the dry reforming of methane, it was decided to conduct a study of the same materials for the partial oxidation of methane with air.

Atmospheric pressure studies showed poor methane conversion, and low CO selectivity and H_2/CO ratio, due to extremely rapid catalyst deactivation (see Fig. 9a) resulting from the oxidation of the initial carbide to MO_2 . This very high reactivity of dioxygen in the oxidation of catalytic phases relative to carbon dioxide is reminiscent of the behaviour of noble metals (66, 67). However, by operating

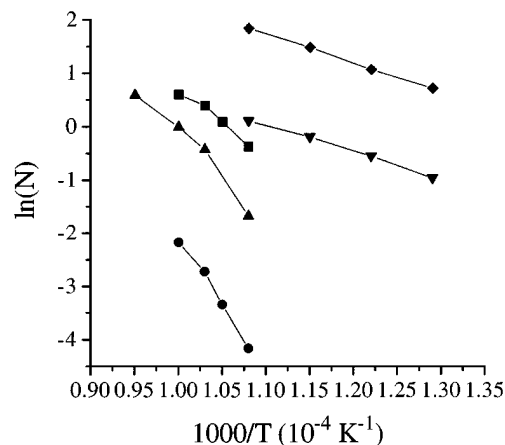


FIG. 7. Pseudo-Arrhenius plots for the methane dry reforming reaction at 2 bar (catalyst weight, 0.071 g Mo_2C ; 0.084 g WC, and 0.05 g remainder, GHSV = $4.4 \times 10^5 \text{ h}^{-1}$, $\text{CH}_4/\text{CO}_2 = 1$). \blacksquare , Mo_2C ; \bullet , WC; \blacktriangle , 5% Ir/ Al_2O_3 ; \blacktriangledown , 5% Rh/ Al_2O_3 ; \blacklozenge , 5% Ru/ Al_2O_3 .

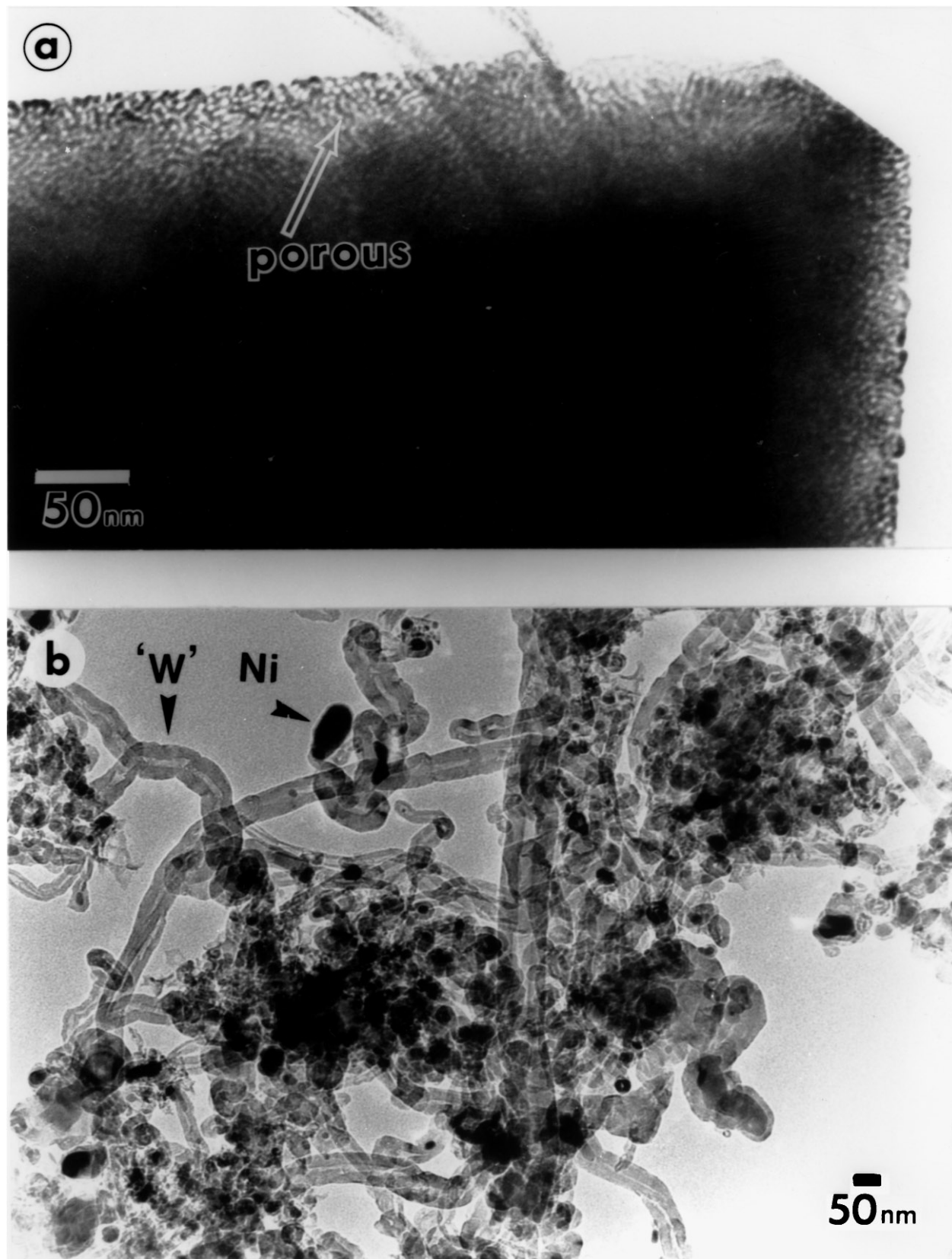


FIG. 8. Electron micrographs of (a) β - Mo_2C and (b) commercial $\text{Ni}/\text{Al}_2\text{O}_3$ (W = whisker carbon), after the dry reforming of methane.

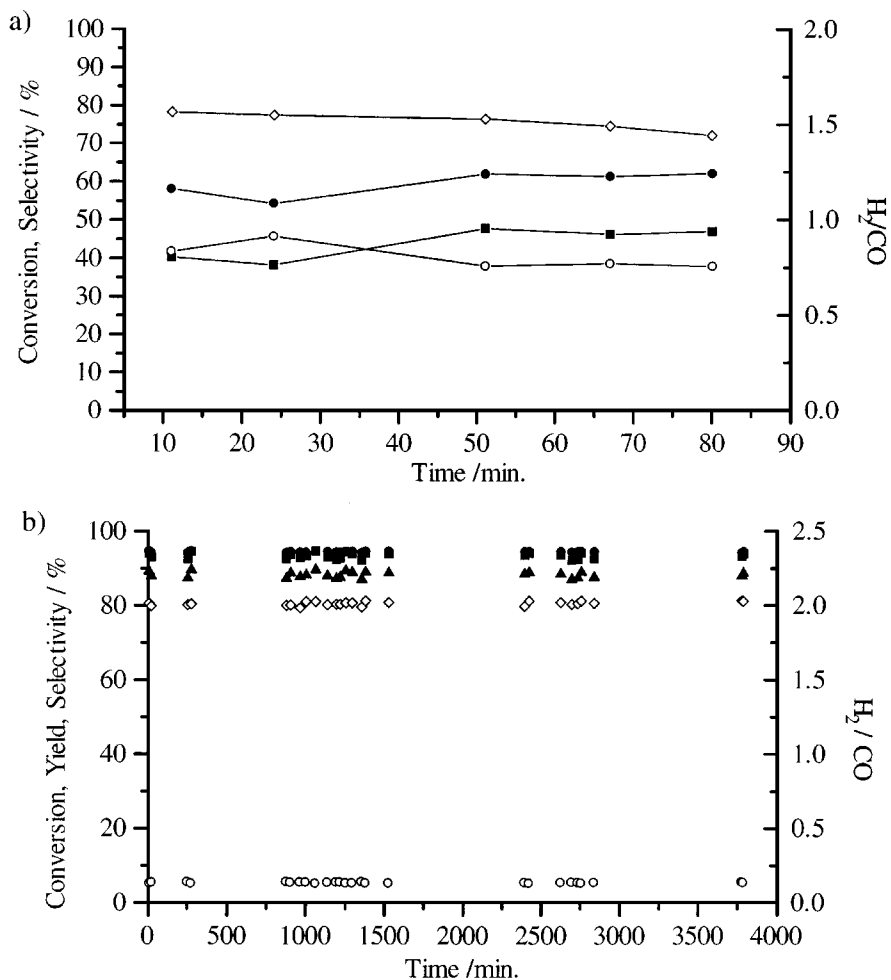


FIG. 9. Lifetime study of β -Mo₂C for the methane partial oxidation reaction ($T = 1170$ K, GHSV = 5.25×10^3 h⁻¹, CH₄/air = 2/5). (a) Atmospheric pressure and (b) 8.7 bar. ■, C[CH₄]; ●, S[CO]; ○, S[CO₂]; ▲, Y[CO]; and ◇, H₂/CO.

at elevated pressure and starting initially with a CH₄/CO₂ mixture, which was switched progressively for CH₄/air over the period of one hour, it is possible to obtain high activities for the partial oxidation of methane, and the results obtained for methane partial oxidation at 1170 K and at elevated pressures over Mo₂C, α -WC and 5 wt% Mo₂C/Al₂O₃ catalysts are listed in Table 3.

TABLE 3

Partial Oxidation of Methane over the Metal Carbide Catalysts
($T = 1170$ K, GHSV = 5.25×10^3 h⁻¹, CH₄/air = 2/5)

Catalyst	P (bar)	C[CH ₄] (%)	S[CO] (%)	S[CO ₂] (%)	Y[CO] (%)	H ₂ /CO
β -Mo ₂ C	4.0 ^a	95	96	5	90	2.01
β -Mo ₂ C	8.7	88	92	8	80	2.02
α -WC	8.7	89	90	10	80	2.05
β -Mo ₂ C/Al ₂ O ₃	8.7	91	92	8	83	2.00

^a Experiment run for only 12 h; no catalyst deactivation.

The catalysts were stable for extended periods of time, e.g., >72 h for β -Mo₂C (see Fig. 9b). In all cases, XRD inspection of the catalysts after reaction showed that the carbide phase was maintained. Further, HRTEM examination of the catalysts after reaction showed no evidence of macroscopic carbon deposition.

Pressure and temperature dependence studies were conducted over a β -Mo₂C catalyst, at pressures varying from 3 to 12 bar and at temperatures between 1070 and 1220 K. The changes in methane conversion, carbon monoxide yield, carbon monoxide selectivity, and carbon dioxide selectivity are shown in Figs. 10 and 11. These show the trends expected from thermodynamics, with Y[CO], S[CO], C[CH₄], and H₂/CO decreasing with increasing pressure and increasing with increasing temperature, while S[CO₂] shows the opposite trend.

Methane Steam Reforming

Methane steam reforming was also investigated over the β -Mo₂C, α -WC, and 5 wt% Mo₂C/Al₂O₃ catalysts at

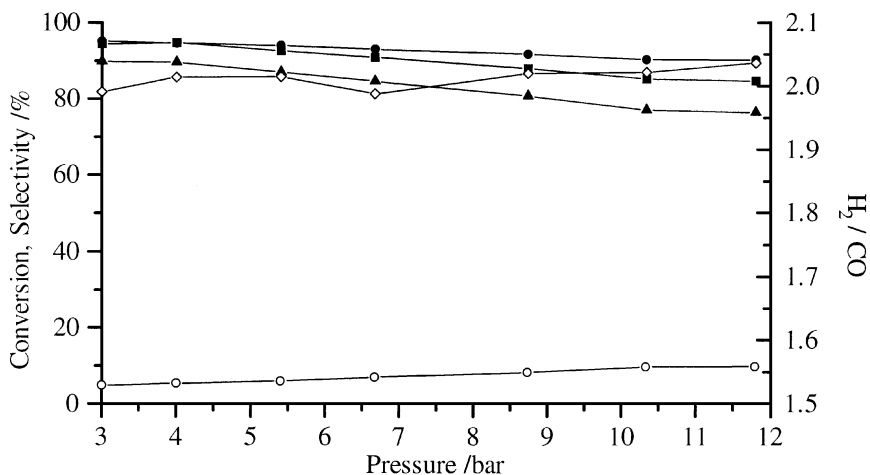


FIG. 10. Pressure effect on the partial oxidation of methane over β -Mo₂C ($T=1170$ K, GHSV = 5.25×10^3 h⁻¹, CH₄/air = 2/5). ■, C[CH₄]; ●, S[CO]; ○, S[CO₂]; ▲, Y[CO]; and ◇, H₂/CO.

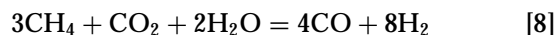
1220 K, and the results obtained are given in Table 4. Initially β -Mo₂C was investigated at low pressure, leading to high conversions. However, as was the case with the dry reforming and partial oxidation, the catalyst deactivated after a period of ≈ 10 h. As before, this was overcome by operation at elevated pressures, resulting in steady activity for the duration of the experiment, as shown in Fig. 12. Postcatalysis XRD showed that the catalyst contained only β -Mo₂C.

α -WC and 5 wt% Mo₂C/Al₂O₃ catalysts were also tested for methane steam reforming at elevated pressures and were also stable and active for the reaction. In all cases HRTEM examination of the catalysts after reaction showed no evidence of macroscopic carbon deposition.

Combined Reforming

In order to demonstrate that the metal carbide catalysts can be used under mixed oxidant conditions and, therefore,

that the reaction conditions could be tuned, the combined methane steam reforming and dry reforming reaction [8] was conducted in a single catalytic bed, over the β -Mo₂C, α -WC, and 5 wt% Mo₂C/Al₂O₃ catalysts.



This was achieved by making a minor modification to the Labcon microreactor described earlier, in order to operate with two catalyst beds. A 5% palladium on alumina catalyst (supplied by Johnson Matthey, powder type 24C, 0.2 g) was placed upstream of the carbide catalyst in a silica U tube. A gas mixture of CH₄/O₂/N₂ of 2/1/4 was passed (GHSV = 5.2×10^3 h⁻¹; 8.7 bar) over the Pd catalyst maintained at 573 K, to convert essentially all of the oxygen present with excess methane to form a product gas mixture of carbon dioxide, water, and unreacted methane. Analysis of this product gas showed C[CH₄] = 26.8%, S[CO₂] =

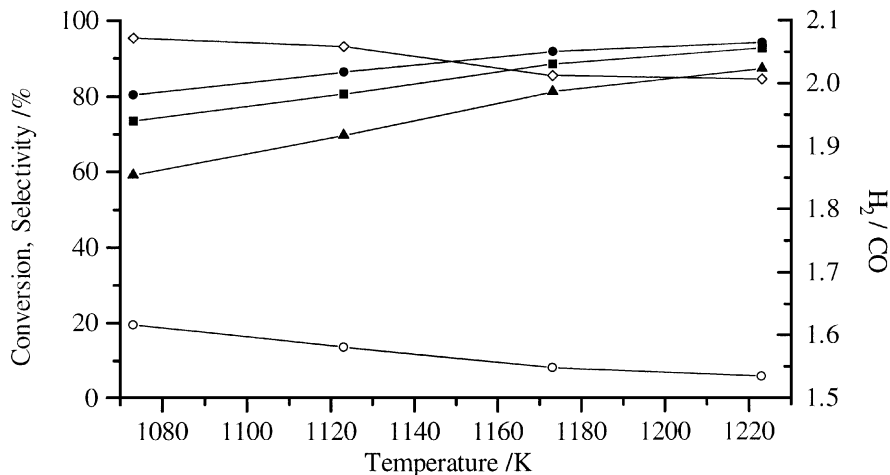


FIG. 11. Temperature effect on the partial oxidation of methane over β -Mo₂C (8.7 bar, GHSV = 5.25×10^3 h⁻¹, CH₄/air = 2/5). ■, C[CH₄]; ●, S[CO]; ○, S[CO₂]; ▲, Y[CO]; and ◇, H₂/CO.

TABLE 4

Steam Reforming of Methane over the Metal Carbide Catalysts
($T = 1220$ K, $\text{GHSV} = 2.87 \times 10^3 \text{ h}^{-1}$, $\text{CH}_4/\text{H}_2\text{O} = 1$)

Catalyst	P (bar)	C[CH ₄] (%)	Y[CO] (%)	H ₂ /CO
β -Mo ₂ C	1.0 ^a	91.5	90.1	3.08
β -Mo ₂ C	8.0	81.8	77.7	3.07
α -WC	8.0	81.9	77.8	3.06
β -Mo ₂ C/Al ₂ O ₃	8.0	82.1	77.9	3.05

^a Catalyst deactivates.

99.1%, S[H₂O] = 96.6%, S[CO] 0.9%, and S[H₂] = 3.4%. This product was immediately heated to 1170 K and passed over the carbide catalyst bed to form a combined dry and steam reforming product (Table 5).

At the elevated pressures used the catalysts were stable for >72 h (Fig. 13), and no macroscopic carbon deposition was observed. The product distribution was that predicted from thermodynamic calculations.

HRTEM Study of the Deactivated Carbides

Figures 14a and 14b show high-resolution electron micrographs of WC, as prepared by CH₄ TPR and after deactivation under dry reforming reaction conditions (1 bar, 1123 K, CH₄/CO₂ = 1), respectively. The precatalysis WC material is polycrystalline, made up of small crystallites which, together, resemble the overall shape and size of the starting metal oxide precursor. This has been reported previously by a number of researchers (68, 69). However, in the deactivated sample the surface of the crystals are composed of tungsten oxide "terraces," although the central bulk of the crystals is still the carbide phase. When WC was treated with CO₂ alone, oxide needles were formed (Fig. 14c). This demonstrates that the favourable oxide formation from the metal carbides can be interrupted by reduction, leading to a shortening of the needles, which then appear as "terraces." If this were occurring under an equilibrium between oxida-

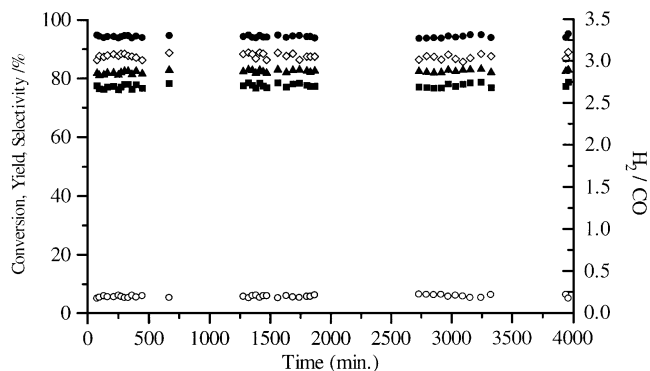


FIG. 12. Lifetime study of β -Mo₂C for the methane steam reforming reaction at 8.0 bar ($T = 1220$ K, $\text{GHSV} = 2.9 \times 10^3 \text{ h}^{-1}$, $\text{CH}_4/\text{H}_2\text{O} = 1$). ■, C[CH₄]; ●, S[CO]; ○, S[CO₂]; ▲, Y[CO]; and ◇, H₂/CO.

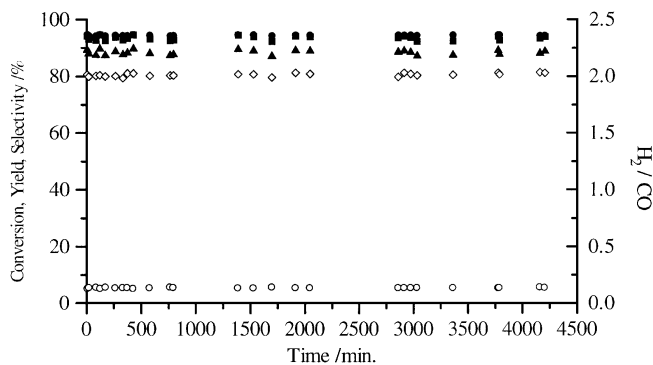


FIG. 13. Lifetime study of α -WC for combined reforming (1170 K, 8.7 bar, $\text{GHSV} = 5.25 \times 10^3 \text{ h}^{-1}$, $\text{CH}_4/\text{CO}_2/\text{H}_2\text{O}/\text{N}_2 = 3/1/2/8$). ■, C[CH₄]; ●, S[CO]; ○, S[CO₂]; ▲, Y[CO]; and ◇, H₂/CO.

tion and recarbidaion, the switching between metal carbide and oxide could be easily imagined.

DISCUSSION

As far back as 1890, it was demonstrated that nickel efficiently catalysed the steam reforming of methane to synthesis gas. Later in 1928 and 1946 its applicability was extended to the analogous reactions of dry reforming and partial oxidation, respectively. While extensively used as a commercial catalyst its major drawback is its propensity to also catalyse the formation of carbon when stoichiometric feedstocks are used. More recently, following initial studies by Ashcroft *et al.* (26, 28), it has been demonstrated that the noble metals (25–30), Rh, Ru, Ir, Pd, and Pt, as well as Re (58), also exhibited high activity and selectivity for the methane reforming reactions under conditions similar to those used for nickel catalysts. These noble metal catalysts offer significant advantages over the conventional Ni catalysts since some of them have a high resistance to carbon formation (30). However, since they are extremely rare and expensive, alternatives are desirable.

It has now been shown that molybdenum and tungsten carbides, synthesised by temperature programming reduction, are highly active catalysts for the methane reforming reactions, despite the oxidative environment that

TABLE 5

Combined Steam and Dry Reforming over the Metal Carbide Catalysts ($T = 1170$ K, $P = 8.7$ bar, $\text{GHSV} = 5.2 \times 10^3 \text{ h}^{-1}$, $\text{CH}_4/\text{CO}_2/\text{H}_2\text{O}/\text{N}_2 = 3/1/2/8$)

Catalyst	C[CH ₄] (%)	S[H ₂] (%)	S[CO] (%)	S[CO ₂] (%)	S[H ₂ O] (%)	H ₂ /CO
Mo ₂ C	91.3	94.9	91.3	8.6	5.1	2.00
α -WC	92.0	93.4	92.4	7.6	6.6	1.97
β -Mo ₂ C/Al ₂ O ₃	90.7	96.1	91.7	8.3	3.9	2.02

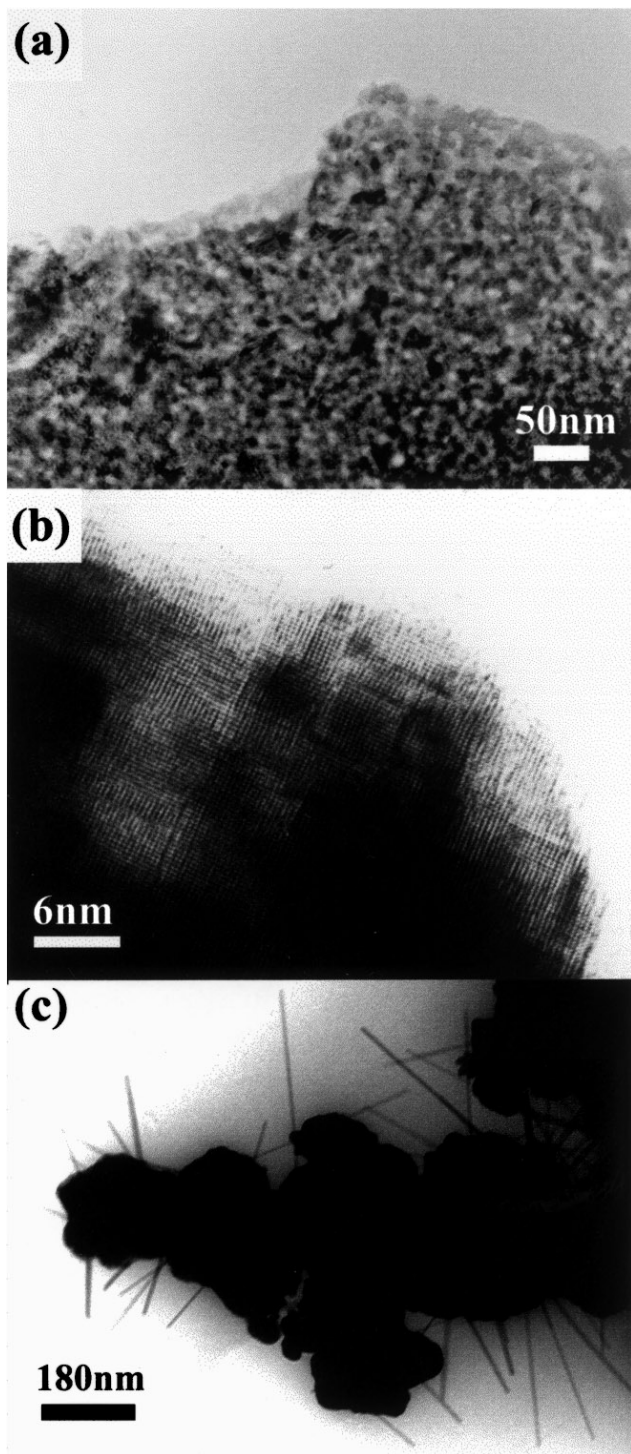
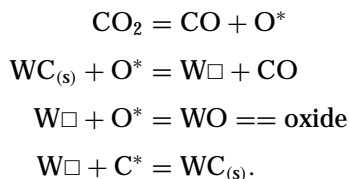


FIG. 14. High-resolution electron micrographs of tungsten carbide and deactivated tungsten carbide. (a) WC, as prepared by CH₄ TPR; (b) WC, deactivated under CH₄/CO₂ = 1; (c) WC, deactivated under CO₂.

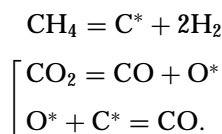
appears to exist in these reactions. Although at elevated pressures the carbide catalysts are extremely stable, at atmospheric pressure and under differential conditions the catalysts deactivate by oxidation to MO₂, slowly in the case

of dry reforming and steam reforming but rapidly in the case of partial oxidation, a trend which reflects the relative strengths of carbon dioxide, water, and oxygen as oxidising agents. Varying the GHSV demonstrated that the rate of oxidation (k_1) is higher than that of recarbination (k_2), or in other words carbon dioxide dissociative adsorption is faster than that for methane. Therefore, under differential conditions the carbides of molybdenum and tungsten are kinetically unstable. The increased catalyst stability at elevated pressures can thus be attributed to the apparently lower GHSV, or a longer contact time, allowing the slower carbination reaction to reach equilibrium. Thus, when the oxidation and carbination reactions are at equilibrium the catalyst remains stable. No changes in the product distributions are observed when the GHSV is varied since the catalyst is operating at thermodynamic equilibrium. Thermodynamic calculations of the dioxygen (O₂) concentration during the dry reforming of methane under stoichiometric feeds ("Chemsage" program) at 1223 K have shown that there is almost no difference between the O₂ partial pressures at ambient and elevated pressures, and therefore deactivation is not attributed to the formation of dioxygen during the dry reforming reaction. If O₂ formation were responsible for catalyst deactivation, the calculations would show that a lower catalyst stability would be expected at elevated pressures: at 1 bar, $p[\text{O}_2] = 5.0 \times 10^{-20}$ bar, and at 8 bar, $p[\text{O}_2] = 2.25 \times 10^{-18}$ bar. Thus it is proposed that deactivation of molybdenum and tungsten carbide at atmospheric pressures is primarily due to kinetic factors. The surface modification of group VI carbides is well known, and Ledoux and co-workers (47) and Iglesia *et al.* (49) have both shown that oxygen-modified carbide surfaces are active catalysts, in their cases for the isomerisation of alkanes. Iglesia explained this by the formation of acidic oxide areas and metallic carbide areas on the surface of the catalysts, leading to bifunctionality, while Ledoux discussed the formation of an intermediate phase, between a carbide and an oxide, named an oxycarbide (48, 51); both these types of oxidised carbide may be present under the reaction conditions, but the conditions present in the reforming of methane allow the surface to cycle, such that the oxide and carbide areas or oxycarbide phase are in dynamic equilibrium with the gas phase.

From the evidence presented it is apparent that reforming reactions over metal carbides can occur via a redox type mechanism. However, we propose that there are two possible competing mechanisms for the formation of synthesis gas. The first is the cycling or redox mechanism and the second is a noble metal type mechanism. In the redox type route, depicted below, it is proposed that after dissociative adsorption of CO₂, the O* produced reacts with carbon in the carbide surface (C_(s)) to leave a vacancy (□). This is then filled with either C*, from methane, retaining the carbide, or O*, a first step in the oxidation to MO₂.



The O^* , however, can also react with C^* formed from the dissociation of methane, instead of carbon from the carbide. This is the basis of the second, noble metal mechanism. This type of mechanism has been previously proposed for supported nickel catalysts, where it was suggested that the active phase was nickel carbide (70, 71). The key steps are



However, since the high reactivity of surface carbide atoms is well established (72, 73) and active carbon species have previously been implicated in the mechanisms for reforming reactions (74–76), it is suggested that both the proposed mechanisms are important in synthesis gas formation; i.e., surface carbon atoms ($\text{C}_{(s)}$) from the carbide and those in excess (C^*) must both participate in the overall reforming reaction. Migration of carbon from the carbide bulk is likely to be too slow to account for the high reforming activities observed, and therefore we do not believe that the bulk (deep) carbide plays a significant role in the reforming reactions over active and stable metal carbide catalysts. This hypothesis is further confirmed when one examines the deactivation of the carbides at atmospheric pressure. As reaction occurs, the catalyst is progressively oxidised along its length (starting with the segment of the bed nearest the gas feed inlet). While enough catalyst remains for the reaction to reach completion, a stable conversion is observed, but this is followed by deactivation when the majority of the catalyst has been oxidised to MoO_2 . If migration of carbon from the bulk were the dominant factor contributing to the reforming reaction, then one would expect to observe metallic Mo or W in postcatalytic XRD patterns for deactivated catalysts (unless diffusion of oxygen into the bulk was comparable or faster), which is not the case. Further, the formation of oxide overlayers is commonly observed for carbides.

The transition metal carbide catalysts used here displayed a very high activity for the dry reforming of methane, on both a per gram basis and per active site. This is crucial if these catalysts are to be suitable for application in industrial reforming. For example, $\beta\text{-Mo}_2\text{C}$ has an activity for dry reforming comparable to that of 5 wt% $\text{Ir}/\text{Al}_2\text{O}_3$ and 5% $\text{Rh}/\text{Al}_2\text{O}_3$ (59), which would imply that Mo_2C is at least as active as standard commercial catalysts and compares very favourably with the activity of the sulfided nickel catalysts currently used to produce reducing gas (24, 29). The order

determined in this study is $\text{Ru} > \text{Rh} > \text{Mo}_2\text{C} > \text{Ir} > \alpha\text{-WC}$; nickel catalysts were not compared since carbon deposition would not allow reliable activity data to be obtained; no such carbon formation occurs on supported ruthenium, rhodium, or iridium catalysts (30). Similar activity trends for the noble metals have been reported previously. The low activity of $\alpha\text{-WC}$, relative to $\beta\text{-Mo}_2\text{C}$, is probably due to the lower surface area of the tungsten carbide material ($\alpha\text{-WC} = 39 \text{ m}^2 \text{ g}^{-1}$; $\beta\text{-Mo}_2\text{C} = 91 \text{ m}^2 \text{ g}^{-1}$), and also may be partly due to the difficulty in obtaining high chemisorption for $\alpha\text{-WC}$ samples, as reported previously (56). However, turnover frequencies reported in the literature for dry reforming over Pt and Pd (29) are less than those for Rh and Ru and in the same region as that for WC.

A number of reasons have been proposed to account for the resistance of tungsten and molybdenum carbides to the formation of coke during reforming. First, it has been shown by Borowiecki and Golebiowski (77) that the oxides of molybdenum and tungsten, when used as dopants in a nickel catalyst for steam reforming, considerably reduce coking during the reforming reaction. The presence of the small amount of oxide on the carbide surface may prevent coking by reaction with adsorbed carbon, before graphitic carbon can be formed. Similarly, the high rate of dissociation of carbon dioxide over the carbides may result in the rapid removal of carbon species, again due to the presence of active oxygen species. In addition, the carbides are already saturated with carbon and hence the dissolution of further carbon to nucleate and form the destructive whiskers (22) so prevalent on nickel catalysts is unlikely.

Finally, the catalytic similarities reported here between the carbides and the noble metals for methane reforming are not surprising since it is well documented (31, 78, 79) that strong electronic similarities exist between these materials.

CONCLUSIONS

In conclusion, the stoichiometric carbon free reforming of methane has been demonstrated using molybdenum and tungsten carbide based catalysts, synthesised by the Boudart TPR method. The carbide catalysts are stable at slightly elevated pressures, and this pressure range is preferable for industrial operations. Further, the conditions used approach those for industrial reformers, particularly those involved in the production of the OXO feed and reducing gas; typical steam reformers operate at 10 to 30 bar, 1120 to 1220 K, and superficial contact times of 0.5 to 1.5 s at STP (80). In addition, molybdenum carbide was found to have a dry reforming activity comparable to that of supported iridium. It seems possible that these cheap, active, and carbon-resistant group VI metal carbide catalysts may have useful applications as alternatives to conventional industrial catalysts, especially for the production of low H_2/CO ratio synthesis gas.

ACKNOWLEDGMENTS

We thank CANMET and the GRI for support for this work. We are also grateful to British Gas plc for awarding a CASE award to J.B.C., and B.P. Chemicals for a CASE award to A.P.E.Y. Dr. C. B. Snowdon (Department of Engineering Science, Oxford) is acknowledged for some helpful discussions, and Akzo-Nobel is thanked for providing the alumina. Finally, we are also grateful to Professor M. P. Brungs and Dr. O. Ostrovski (University of New South Wales, Australia) for carrying out the thermodynamic calculations of the oxygen concentrations.

REFERENCES

- Cornot-Gandolphe, S., *Energy Exploration & Exploitation* **13**, 3 (1995).
- Leprince, P., and Valais, M., *Energy Sources* **15**, 95 (1993).
- Fox, J. M., III, *Catal. Rev.-Sci. Eng.* **35**, 169 (1993).
- Foster, N. R., *Appl. Catal.* **19**, 1 (1985).
- Gesser, H. D., Hunter, N. R., and Prakash, C. P., *Chem. Rev.* **85**, 235 (1985).
- Durante, V. A., Walker, D. W., Gussow, S. M., and Lyons, J. E., Sun Refining and Marketing Company, U.S. Patent 4,918,249 (1990).
- Periana, R. A., Taube, D. J., Evitt, E. R., Löffler, D. G., Wentrcek, P. R., Voss, G., and Masuda, T., *Science* **259**, 340 (1993).
- Otsuka, K., Komatsu, T., Jinno, K., Uragami, Y., and Morigawa, A., in "Proc. 9th Int. Cong. on Catalysis" (M. J. Phillips and M. Ternan, Eds.), Vol. II, p. 915. Chemical Institute of Canada, Ottawa, 1988.
- Baldwin, T. R., Burch, R., Squire, G. D., and Tsang, S. C., *Appl. Catal.* **74**, 137 (1991).
- Claridge, J. B., Green, M. L. H., Tsang, S. C., and York, A. P. E., *Appl. Catal.* **89**, 103 (1992).
- York, A. P. E., Green, M. L. H., Claridge, J. B., and Tsang, S. C., *Stud. Surf. Sci. Catal.* **83**, 315 (1994).
- Green, M. L. H., Tsang, S. C., Vernon, P. D. F., and York, A. P. E., *Catal. Lett.* **13**, 341 (1992).
- Green, M. L. H., Tsang, S. C., Vernon, P. D. F., and York, A. P. E., *Ind. Eng. Chem. Res.* **32**, 1030 (1993).
- Labinger, J. A., and Ott, K. C., *J. Phys. Chem.* **91**, 2682 (1987).
- Labinger, J. A., *Catal. Lett.* **1**, 371 (1988).
- Hinson, P. G., Clearfield, A., and Lunsford, J. H., *J. Chem. Soc. Chem. Commun.* 1430 (1991).
- Sofranko, J. A., Leonard, J. J., Jones, C. A., Gaffney, A. M., and Withers, H. P., *Catal. Today* **3**, 127 (1988).
- Burch, R., Squire, G. D., and Tsang, S. C., *Appl. Catal.* **46**, 69 (1989).
- Jiang, Z.-C., Yu, C.-J., Fang, X.-P., Li, S.-B., and Wang, H.-L., *J. Phys. Chem.* **97**, 12,870 (1993).
- Otsuka, K., Jinno, K., and Morikawa, A., *J. Catal.* **100**, 353 (1986).
- Kuo, J. C. W., and Kresge, C. T., *Catal. Today* **4**, 463 (1989).
- Rostrup-Nielsen, J. R., in "Catalysis Science and Technology" (J. R. Anderson and M. Boudart, Eds.), Vol. 5, p. 1. Springer-Verlag, Berlin, 1984.
- Sie, S. T., Senden, M. M. G., and Wechem, H. M. H., *Catal. Today* **8**, 371 (1991).
- Rostrup-Nielsen, J. R., *J. Catal.* **85**, 31 (1984).
- Rostrup-Nielsen, J. R., *J. Catal.* **31**, 173 (1973).
- Ashcroft, A. T., Cheetham, A. K., Foord, J. S., Green, M. L. H., Grey, C. P., Murrell, A. J., and Vernon, P. D. F., *Nature* **344**, 319 (1990).
- Vernon, P. D. F., Green, M. L. H., Cheetham, A. K., and Ashcroft, A. T., *Catal. Lett.* **6**, 181 (1990).
- Ashcroft, A. T., Cheetham, A. K., Green, M. L. H., and Vernon, P. D. F., *Nature* **352**, 225 (1991).
- Rostrup-Nielsen, J. R., and Bak Hansen, J.-H., *J. Catal.* **144**, 38 (1993).
- Claridge, J. B., Green, M. L. H., Tsang, S. C., York, A. P. E., Ashcroft, A. T., and Battle, P. D., *Catal. Lett.* **22**, 299 (1993).
- Levy, R. B., and Boudart, M., *Science* **181**, 547 (1973).
- Leclercq, L., in "Surface Properties and Catalysis by Non-metals" (J. P. Bonnelle, Ed.), p. 433. 1983.
- Oyama, S. T., and Haller, G. L., *Catalysis* **3**, 333 (1982).
- Volpe, L., and Boudart, M., *J. Solid State Chem.* **59**, 348 (1985).
- Zeng, D., and Hampden-Smith, M. J., *Chem. Mater.* **4**, 968 (1992).
- Lee, J. S., Oyama, S. T., and Boudart, M., *J. Catal.* **106**, 125 (1987).
- Lee, J. S., Volpe, L., Ribeiro, F. H., and Boudart, M., *J. Catal.* **112**, 44 (1988).
- Ledoux, M. J., and Pham-Huu, C., *Catal. Today* **15**, 263 (1992).
- Oyama, S. T., Schlatter, J. C., Metcalfe, J. E., III, and Lambert, J. M., Jr., *Ind. Eng. Chem. Res.* **27**, 1639 (1988).
- Lemaitre, J., Vidick, B., and Delmon, B., *J. Catal.* **99**, 415 (1986).
- Sherif, F., and Vreugdenhil, W., in "The Chemistry of Transition Metal Carbides and Nitrides" (S. T. Oyama, Ed.), p. 414. Blackie, Glasgow, 1996.
- Schlatter, J. C., Oyama, S. T., Metcalfe, J. E., III, and Lambert, J. M., Jr., *Ind. Eng. Chem. Res.* **27**, 1648 (1988).
- Lee, J. S., and Boudart, M., *Appl. Catal.* **19**, 207 (1985).
- Abe, H., and Bell, A. T., *Catal. Lett.* **18**, 1 (1993).
- Choi, J.-G., Brenner, J. R., and Thompson, L. T., *J. Catal.* **154**, 33 (1995).
- Ledoux, M. J., Pham-Huu, C., Marin, S., Weibel, M., and Guille, J., *C. R. Acad. Sci. Paris II* **310**, 707 (1990).
- Ledoux, M. J., Pham-Huu, C., York, A. P. E., Blekkan, E. A., Delporte, P., and Del Gallo, P., in "The Chemistry of Transition Metal Carbides and Nitrides" (S. T. Oyama, Ed.), p. 373. Blackie, Glasgow, 1996.
- Iglesia, E., Ribeiro, F. H., Boudart, M., and Baumgartner, J. E., *Catal. Today* **15**, 307 (1992).
- Iglesia, E., Ribeiro, F. H., Boudart, M., and Baumgartner, J. E., *Catal. Today* **15**, 455 (1992).
- Blekkan, E. A., Pham-Huu, C., Ledoux, M. J., and Guille, J., *Ind. Eng. Chem. Res.* **33**, 1657 (1994).
- Pham-Huu, C., Ledoux, M. J., and Guille, J., *J. Catal.* **143**, 249 (1993).
- Pham-Huu, C., York, A. P. E., Benaissa, M., Del Gallo, P., and Ledoux, M. J., *Ind. Eng. Chem. Res.* **34**, 1107 (1995).
- Park, K. Y., Seo, W. K., and Lee, J. S., *Catal. Lett.* **11**, 349 (1991).
- Leclercq, L., Almazouari, A., Dufour, M., and Leclercq, G., in "The Chemistry of Transition Metal Carbides and Nitrides" (S. T. Oyama, Ed.), p. 345. Blackie, Glasgow, 1996.
- Woo, H. C., Park, K. Y., Kim, Y. G., Nam, I.-S., Chung, J. S., and Lee, J. S., *Appl. Catal.* **75**, 267 (1991).
- Ribeiro, F. H., Dalla Betta, R. A., Guskey, G. J., and Boudart, M., *Chem. Mater.* **3**, 805 (1991).
- Lee, J. S., Lee, K. H., and Lee, J. Y., *J. Phys. Chem.* **96**, 362 (1992).
- Claridge, J. B., Green, M. L. H., and Tsang, S. C., *Catal. Today* **21**, 455 (1994).
- York, A. P. E., Claridge, J. B., Brungs, A. J., Tsang, S. C., and Green, M. L. H., *J. Chem. Soc. Chem. Commun.* 39 (1997).
- Gadalla, A. M., and Sommer, M. E., *J. Am. Ceram. Soc.* **72**, 683 (1989).
- Yamazaki, O., Nozkai, T., Omata, K., and Fujimoto, K., *Chem. Lett.* 1953 (1992).
- Audier, M., Oberlin, A., Oberlin, M., Coulon, M., and Bonnetain, L., *Carbon* **19**, 217 (1981).
- Bowker, M., Cassidy, T. J., Ashcroft, A. T., and Cheetham, A. K., *J. Catal.* **143**, 308 (1993).
- Oyama, S. T., *Catal. Today* **15**, 179 (1992).
- Oyama, S. T., in "The Chemistry of the Transition Metal Carbides and Nitrides" (S. T. Oyama, Ed.), p. 1. Blackie, Glasgow, 1996.
- Mallens, E. P. J., Hoebink, J. H. B. J., and Marin, G. B., *Catal. Lett.* **33**, 291 (1995).
- Buyevskaya, O. V., Wolf, D., and Baerns, M., *Catal. Lett.* **29**, 249 (1994).
- Claridge, J. B., Brungs, A. J., and Green, M. L. H., *Chem. Mater.*, in press.
- Lee, J. S., *Korean J. Chem. Eng.* **6**, 196 (1989).

70. Kroll, V. C. H., Swaan, H. M., Lacombe, S., and Mirodatos, C., *J. Catal.* **167**, 387 (1997).
71. Schuurman, Y., Marquez-Alvarez, C., Kroll, V. C. H., and Mirodatos, C., *Catal. Today*, in press.
72. Gihiland, E. R., and Harriott, P., *Ind. Eng. Chem. Res.* **11**, 2195 (1954).
73. Ribeiro, F. H., Dalla-Betta, R. A., Boudart, M., Baumgartner, J., and Iglesia, E., *J. Catal.* **130**, 86 (1991).
74. Kneale, B., and Ross, J. R. H., *Farad. Disc. Chem. Soc.* **72**, 157 (1981).
75. Kneale, B., and Ross, J. R. H., *J. Chem. Soc. Chem. Commun.* 751 (1981).
76. Mark, M. F., and Maier, W. F., *Angew. Chem. Int. Ed. Engl.* **33**, 1657 (1994).
77. Borowiecki, T., and Golebiowski, A., *Catal. Lett.* **25**, 309 (1994).
78. Eberhart, M. E., and Maclaren, J. M., in "The Chemistry of the Transition Metal Carbides and Nitrides" (S. T. Oyama, Ed.), p. 107. Blackie, Glasgow, 1996.
79. Guillermet, A. F., Haglund, J., and Grimwall, G., *Phys. Rev. B* **45**, 11,557 (1992).
80. Ridler, D. E., and Twigg, M. V., in "Catalyst Handbook" (M. V. Twigg, Ed.), p. 225. Wolfe Publishing, London, 1989.