

Molybdenum and tungsten carbides as catalysts for the conversion of methane to synthesis gas using stoichiometric feedstocks

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Molybdenum and tungsten carbides are extremely active and stable catalysts for the dry reforming, partial oxidation and steam reforming of methane to synthesis gas using stoichiometric feedstock; no bulk carbon deposition was observed.

Recent estimates indicate that world reserves of natural gas will outlast those of oil by a considerable period.¹ Current industrial use of methane as a chemical feedstock proceeds by initial conversion to carbon monoxide and hydrogen (synthesis gas) by either steam reforming² [eqn. (1)] (a large scale process) or by dry reforming, [eqn (2)]; a further route is *via* partial oxidation [eqn. (3)].



Nickel catalysts are used industrially for both the methane steam and dry reforming reactions because of their fast turnover rates, long term stability and low cost.² However, they have a major drawback since the nickel catalysts also catalyse carbon formation *via* methane decomposition and CO disproportionation, both of which lead to catalyst deactivation and the plugging of the reformer tubes by carbon deposits. Thus, in practice large excesses of oxidants are used in order to prevent carbon deposition. This results in synthesis gas with H₂/CO and CO₂/CO ratios which are not optimal for further conversion to major end products, such as methanol or gasoline. Considerable effort has been concentrated on exploring catalysts for eqns. (1)–(3) which are resistant to carbon formation at or near stoichiometric reactant ratios. Previously, sulfur passivated nickel catalysts³ and noble metal catalysts^{4–7} have been shown to exhibit kinetic resistance to carbon formation, but the low activities of sulfur passivated nickel and the high costs and limited availability of the noble metals have limited their application.

In the last 20 years, group VI transition metal carbides have been found to be active catalysts, comparable to platinum group metal catalysts for a number of reactions. Here we describe new catalysts, based on carbides of molybdenum and tungsten, for the reforming of methane using stoichiometric feedstocks at slightly elevated pressures. No carbon deposition is observed, and the consequential selectivities and conversions to carbon monoxide and hydrogen are those predicted by thermodynamic considerations.

The high surface area carbide catalysts were prepared by temperature programmed reduction of the oxides or supported oxides in a flow of methane or methane–hydrogen mixture, as previously described for β-Mo₂C,⁸ WC⁹ and Mo₂C/Al₂O₃.¹⁰ Normally the catalysts were prepared *in situ* and tested immediately.

Table 1 shows the results obtained for the dry reforming of methane to synthesis gas with carbon dioxide, using β-Mo₂C (S_g = 91 m² g⁻¹) and WC (S_g = 39 m² g⁻¹) as catalysts at both ambient and elevated pressure. The initial synthesis gas yields very closely approach those predicted from thermodynamic considerations, if carbon deposition is discounted.⁷ At ambient

pressure catalyst deactivation occurred, and this was clearly observable after 8 h [Fig. 1(a)]. Powder XRD (not given) showed that the initial β-Mo₂C was converted to MoO₃, which has only very low activity for methane dry reforming. However, when the experiment was run at slightly elevated pressure

Table 1 Catalytic performance of molybdenum and tungsten carbides for various methane reforming reactions

Catalyst	CH ₄ : oxidant	Pressure/ bar	T/K	C[CH ₄] ^a (%)	Y[CO] ^b (%)	H ₂ /CO ^c
β-Mo ₂ C	1:1 ^d	1.0	1120	92.4	92.5	0.93
β-Mo ₂ C	1:1 ^d	8.3	1120	62.5	69.5	0.78
WC	1:1 ^d	8.3	1120	62.7	68.7	0.79
5% Mo ₂ C/Al ₂ O ₃	1:1 ^d	8.3	1120	65.2	70.1	0.81
β-Mo ₂ C	2:1 ^e	4.0	1170	94.7	89.6	2.01
β-Mo ₂ C	2:1 ^e	8.7	1170	88.0	80.7	2.02
WC	2:1 ^e	8.7	1170	87.5	78.2	2.04
5% Mo ₂ C/Al ₂ O ₃	2:1 ^e	8.7	1170	90.6	82.5	2.00
β-Mo ₂ C	1:1 ^f	1.0	1220	91.5	90.1	3.08
β-Mo ₂ C	1:1 ^f	8.3	1220	81.8	77.7	3.07
WC	1:1 ^f	8.3	1220	81.9	77.8	3.06
5% Mo ₂ C/Al ₂ O ₃	1:1 ^f	8.3	1220	82.1	77.9	3.05

^a C[CH₄] = (% conversion of CH₄ into all products). ^b Y[CO] = amount of CO in products/(amount (C) in reagents). ^c H₂/CO = (amount of H₂ in products)/(amount of CO in products). ^d Dry reforming with carbon dioxide (inlet GHSV = 2.8 × 10³ h⁻¹). ^e Partial oxidation with air (inlet GHSV = 5.2 × 10³ h⁻¹). ^f Steam reforming with water (inlet GHSV = 2.8 × 10³ h⁻¹).

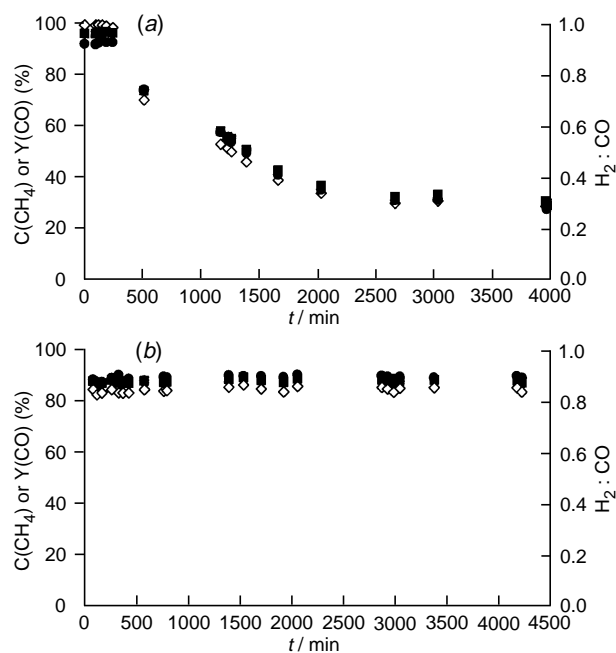


Fig. 1 Catalyst stabilities for the dry reforming of methane ($T = 1220 \text{ K}$; $\text{CH}_4:\text{CO}_2 = 1$; $\text{GHSV} = 2.8 \times 10^3 \text{ h}^{-1}$); (a) pressure = 1 atm; (b) pressure = 8.3 atm; (■) Y[CO], (◇) C[CH₄], (●) H₂:CO

(about 8 bar), high activity was maintained for the duration of the experiments (typically 144 h), with no observable deterioration in the catalysts [Fig. 1(b)] providing, at least, an initial idea of the long term stability of the catalysts, although longer experiments need to be conducted. XRD studies of the quenched catalyst after use showed no trace of MoO_2 . Further, a high resolution transmission electron microscopy (HRTEM) study of the pre- and post-catalysis samples indicated that no bulk carbon deposition had occurred on the catalyst. In contrast, HRTEM examination of used nickel catalysts show the presence of large amounts of whisker carbon.⁴ Activity studies of our carbide catalysts and of supported noble metal catalysts, for the dry reforming of methane under differential conditions (*i.e.* conversion kept < 10%), show that $\beta\text{-Mo}_2\text{C}$ has comparable activity on a gram basis to that of 5% Ir- Al_2O_3 , which is well known as an active catalyst for steam and dry reforming.⁵ Indeed, the relative activity of a number of the reforming catalysts has been established as: $\text{Ru} > \text{Rh} > \text{Ir} \approx \text{Mo}_2\text{C} > \text{WC} > \text{Pd} > \text{Pt}$.^{5,11,12}

Table 1 also shows the results obtained for $\beta\text{-Mo}_2\text{C}$, WC and $\text{Mo}_2\text{C-Al}_2\text{O}_3$ as catalysts for the partial oxidation and steam reforming reactions, also at slightly elevated pressures. Again the reaction yields approach predicted thermodynamic equilibrium values, and have been carried out for 72 h or more without any evidence of macroscopic carbon deposition or catalyst deactivation. In the corresponding reactions at ambient pressure, catalyst deactivation was always observed due to the formation of inactive MoO_2 .

The stabilisation of the active metal carbide phase under slightly elevated pressures is surprising since, although the carbides can be synthesised from the oxides by methane at high temperatures (> 1000 K), they are very reactive towards oxidation by oxygen, carbon dioxide and water.

We can offer no clear reasons to account for the high catalytic activity of the early transition metal carbides for the methane reforming reactions, nor for their resistance to macroscopic carbon formation. However, catalytic similarities between early

transition metal carbides and the noble metals, which are active for steam reforming, have been noted before.¹³⁻¹⁶

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