Comparison of the group V and VI transition metal carbides for methane dry reforming and thermodynamic prediction of their relative stabilities

Attila J. Brungs, Andrew P.E. York and Malcolm L.H. Green

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

Received 7 October 1998; accepted 17 December 1998

The group V and VI transition metal carbides have been prepared by CH_4 TPR, and tested for the dry reforming of methane with carbon dioxide, at elevated pressure. Mo_2C and WC were the most stable catalysts, while the group V metal carbides showed the stability order: vanadium $>$ niobium $>$ tantalum. Catalyst deactivation was due to carbide oxidation with CO_2, while stability was associated with the reaction of metal oxide (from deactivation) with CH_4, giving the metal carbide. Calculation of the Gibbs free energy for this reaction resulted in a predicted catalyst stability trend similar to that obtained experimentally.

Keywords: methane, synthesis gas, dry reforming, transition metal carbides

1. Introduction

Last year, York et al. [1] demonstrated that the carbides of molybdenum and tungsten were potential alternatives to the group VIII metals as catalysts for the reforming of methane to synthesis gas with steam, carbon dioxide or air/oxygen (see table 1, dark shading). These new catalysts were highly active and stable under certain conditions, and the success of their application to methane reforming was attributed to the similarities between these carbides and Ru and Pt, respectively [2–5]. It was also recently demonstrated, following the syntheses of the high surface area carbides of vanadium [6], niobium [7,8] and tantalum [9], using the temperature-programmed reduction (TPR) method, that transition metal carbides other than those of group VI elements also exhibit catalytic properties somewhat analogous to those of the group VIII metals [10–12]. For example, Chen discovered that while the interaction of n-butane was very limited with clean vanadium surfaces, when passed over vanadium carbide large scale decomposition occurred [12], again this behaviour is similar to that with platinum.

In this paper, we compare the catalytic activity and stability of the group V transition metal carbides, synthesised by the relatively well developed TPR reaction of metal oxide with methane and hydrogen, with the carbides of the group VI metals. Some thermodynamic calculations are also presented, which explain the stability differences observed for the various carbides.

2. Experimental

2.1. Catalyst synthesis and characterisation

The high surface area metal carbide materials were prepared using the method pioneered by Boudart and his coworkers, i.e., TPR [13]. The relevant oxides, i.e., MoO_3, WO_3, V_2O_5, Nb_2O_5 and Ta_2O_5, were reacted in a flow of 20% v/v CH_4/H_2 (150 $ml\,min^{-1}$), and the temperature increased from room temperature to 1023–1223 K, depending on the metal oxide, at a heating rate of 1 $K\,min^{-1}$. Normally the catalysts were prepared *in situ* and tested immediately. *Ex situ* analysis of the high surface area carbides was carried out after passivation in flowing 1% O_2/N_2 for 10 h at room temperature, since these materials are readily and exothermically oxidised in air.

The crystalline components of the materials were identified by X-ray diffraction (XRD) using a Philips PW1710 diffractometer with Cu Kα radiation. Catalyst surface areas were determined using an all glass high vacuum line and calculated from the N_2 BET isotherms.

2.2. Catalyst testing and product analysis

The apparatus used in this work was a modified version of the commercial Labcon microreactor described previously [14]. Briefly, the reactor was constructed of $1/8''$ and $1/16''$ o.d. 316 stainless-steel tubing and 316 stainless-steel Swagelok fittings throughout. The catalyst sample 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 temperature

Table 1
Transition metals successfully applied to methane reforming (shaded dark grey) (Mo and W are active as bulk carbides).

Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
La	Hf	Ta	W	Re	Os	Ir	Pt

controller. Gas flow rates were controlled using Brooks 5850TR mass flow controllers and the exit gas stream from the reactor passed through a Tescom two-stage 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%.

3. Results and discussion

3.1. Catalyst characterisation and testing

The XRD patterns and BET surface areas of the metal carbides, synthesised by TPR of the metal oxides with CH_4/H_2, were obtained, and some of the important points are summarised in table 2. In all cases, the pure single-phase carbides were prepared, cubic in the case of the group V carbides and hexagonal for the group VI carbides, while none of the starting oxide could be seen; the cell parameters were in very good agreement with the literature values (shown below in parentheses) [15]: $VC_{0.73–0.97}$, $a_0 = 0.4166$ nm (0.4131–0.4165); $NbC_{0.7–0.99}$, $a_0 = 0.4469$ nm (0.4431–0.4471); $TaC_{0.7–0.99}$, $a_0 = 0.4450$ nm (0.4410–0.4455); β-Mo_2C, $a_0 = 0.3000$ nm (0.3006); and α-WC, $a_0 = 0.2910$ nm (0.2906). While it is difficult to state the exact value of x for the group V metal carbides, the XRD data indicate that the value lies close to 1.

Table 2
Summary of some of the characteristics of the metal carbides.

Oxide precursor	Carbide phase	Structure	Final T (K)	S_g ($m^2\,g^{-1}$)
MoO_3	β-Mo_2C	hcp	1020	91
WO_3	α-WC	hex.	1150	39
V_2O_5	VC_x[a]	fcc	1173	44
Nb_2O_5	NbC_x	fcc	1173	62
Ta_2O_5	TaC_x	fcc	1223	54

[a] $x = 0.73–0.97$ (VC_x); 0.70–0.99 (NbC_x) and (TaC_x) [15].

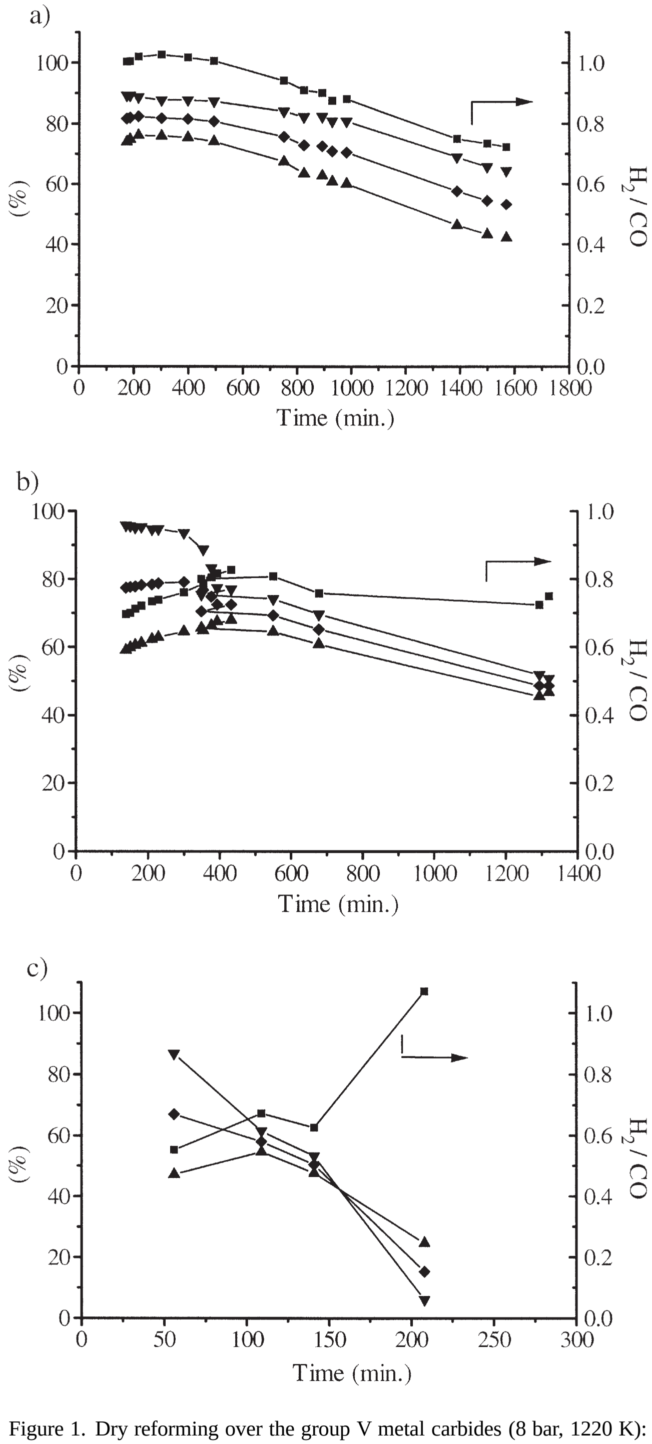


Figure 1. Dry reforming over the group V metal carbides (8 bar, 1220 K): (a) VC (GHSV $= 1.8 \times 10^3\ h^{-1}$), (b) NbC ($1.2 \times 10^3\ h^{-1}$), and (c) TaC ($1.6 \times 10^3\ h^{-1}$). (▲) CH_4 conversion; (▼) CO_2 conversion; (♦) CO yield; and (■) H_2/CO ratio.

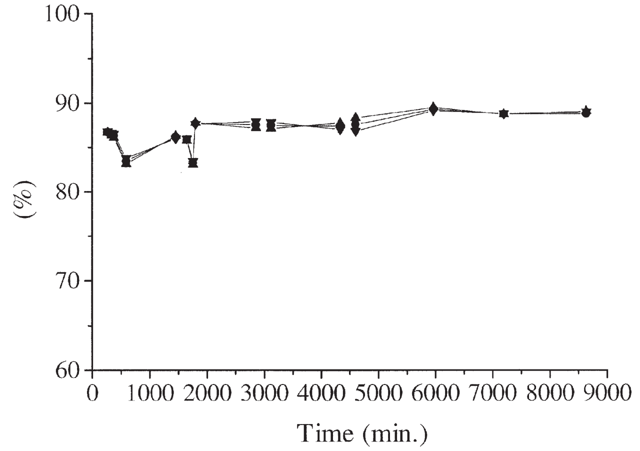


Figure 2. Lifetime test for the dry reforming of methane over β-Mo_2C (1220 K, 8.1 bar, GHSV = 2.2×10^3 h^{-1}). (▲) CH_4 conversion; (▼) CO_2 conversion; and (●) CO yield.

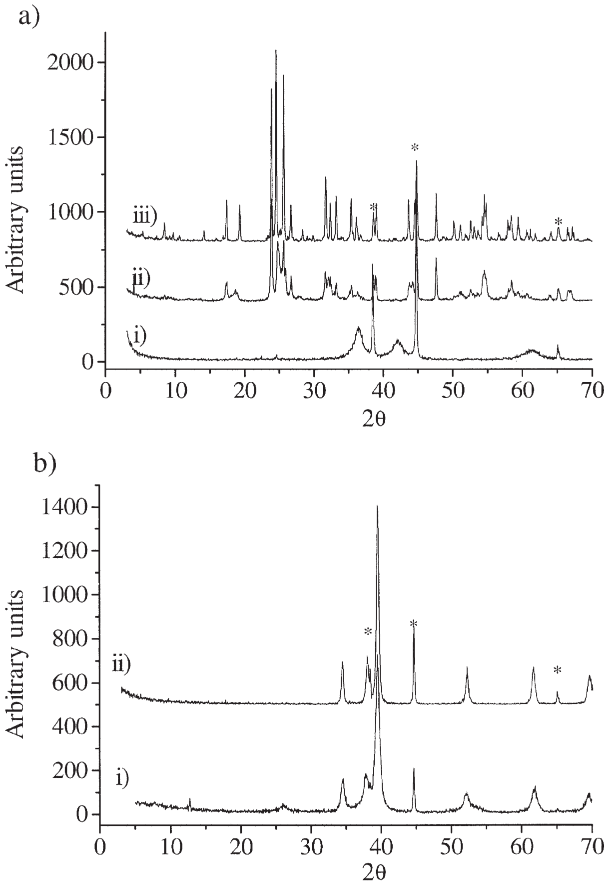


Figure 3. XRD patterns of the (a) NbC and (b) Mo_2C systems (* = Al): (i) carbides as prepared by CH_4 TPR; (ii) post-dry reforming; and (iii) pure Nb_2O_5.

The metal carbides were then tested as catalysts for synthesis gas production by the dry reforming of methane with carbon dioxide. It was previously shown that Mo_2C and WC were stable and active catalysts at elevated pressures [1,16], using stoichiometric feedstocks, and, therefore, elevated pressures were employed for testing of the group V metal carbides. The conditions used for the group V metal carbides were as follows: temperature 1220 K, pressure 8 bar, and CH_4/CO_2 ratio 1. The gas hourly space velocity varied slightly from catalyst to catalyst due to differences in precursor oxide density. Figure 1 (a)–(c) shows that all three group V transition metal carbides deactivated with time on stream, while Mo_2C was stable for 5 days (figure 2) with no sign of any deactivation (similar results have been obtained for WC (not shown)), despite the higher GHSV used for this catalyst. VC appeared to be stable for almost 10 h, while TaC deactivated so rapidly that no significant catalytic activity for dry reforming was observed. Thus, the order of stability which can be observed within the group V and VI transition metal carbides for methane dry reforming corresponds to:

$$Mo_2C \approx WC > VC > NbC > TaC$$

Figure 3 (a) and (b) shows the XRD patterns for pre- and post-catalytic samples of NbC and Mo_2C. In the case of NbC, it can be seen that the carbide phase has been converted almost entirely to the oxide (Nb_2O_5 also shown for comparison), while no oxide peaks have appeared in the pattern for Mo_2C and no phase changes are apparent. VC and TaC gave similar results to the NbC sample, while WC was similar to Mo_2C and, therefore, XRD patterns for these catalysts are not given.

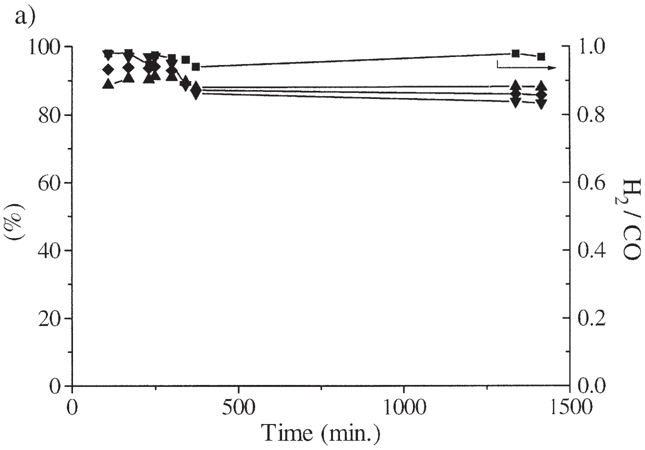
Stabilisation of NbC was attempted by employing higher reaction temperatures for the dry reforming reaction, and figure 4 (a) and (b) shows the results obtained at 1320 and 1370 K. It can be seen that the increase in reaction temperature did indeed lead to a stabilisation of the niobium carbide catalyst system. At 1320 K, NbC displayed a high conversion of methane and carbon dioxide; however, the significant presence of oxide peaks in the post-catalysis XRD pattern, shown in figure 5, pattern (ii), indicated that the system was not stable and would have eventually deactivated. At 1370 K, the XRD pattern exhibits no traces of oxide (figure 5, pattern (iii)), the catalyst remaining entirely in the carbide form. However, at this temperature, there is a significant contribution from gas-phase reactions, and the high H_2/CO ratio (1.3–1.45), shown in figure 4(b), indicates that carbon deposition is occurring. In addition, it should be noted that the carbide peaks were much sharper after reaction at 1370 K, suggesting that sintering had occurred, as would be expected at this high temperature.

Coking is not a problem over the metal carbide catalysts, as has been shown before [16]. Thus, it would appear that the carbide catalysts deactivate via an oxidation process involving carbon dioxide (reaction (1)), probably by dissociative adsorption of CO_2 [17,18], followed by oxidation of the carbide by oxygen atoms. The transformation of the oxide back into the carbide (via reaction (2)) is probably of fundamental importance to catalyst stabilisation and is promoted by higher temperatures.

For example, for molybdenum:

$$Mo_2C + 5CO_2 \rightleftharpoons 2MoO_2 + 6CO \qquad (1)$$

$$2MoO_2 + 5CH_4 \rightleftharpoons Mo_2C + 4CO + 10H_2 \qquad (2)$$



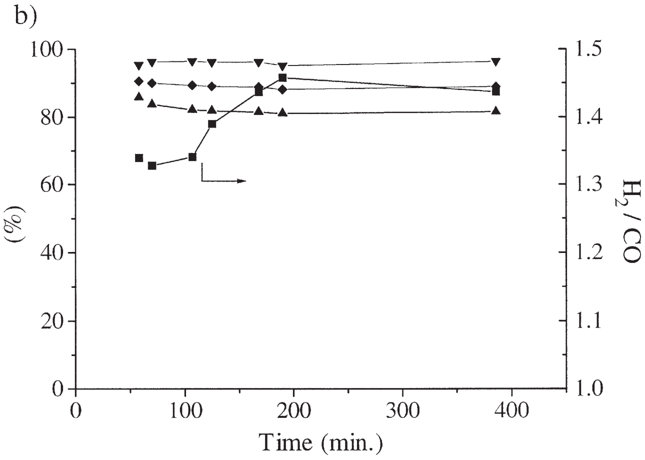


Figure 4. Methane dry reforming over NbC (8 bar, 1.2×10^3 h^{-1}): (a) 1320 K and (b) 1370 K. (▲) CH_4 conversion; (▼) CO_2 conversion; (◆) CO yield; and (■) H_2/CO ratio.

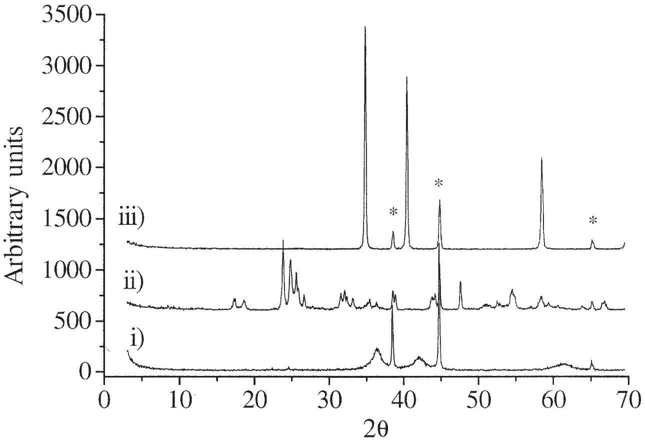


Figure 5. XRD patterns of the NbC catalyst system (∗ = Al): (i) as prepared; (ii) post-dry reforming at 1320 K; and (iii) post-dry reforming at 1370 K.

In other words, oxidation and reduction (or recarbidation) are in competition, and catalyst deactivation is due to the relative stability of the metal oxide or instability of the metal carbide under the dry reforming conditions.

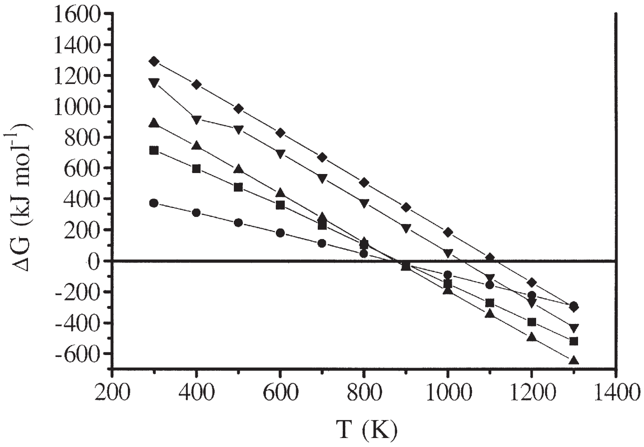


Figure 6. Calculated Gibbs free energies for the general reaction (3). (■) Mo_2C; (●) WC; (▲) VC; (▼) NbC; (◆) TaC.

3.2. Thermodynamic considerations

To confirm the importance of the recarbidation reaction to catalyst stability, the Gibbs free energies for the general reaction (3) were calculated for a range of temperatures for the five transition metal carbides under investigation, using standard thermodynamic data [19]:

$$zM_xO_y + (x + yz)CH_4 \rightleftharpoons xM_zC + yzCO + 2(x + yz)H_2 \qquad (3)$$

The ΔG obtained are summarised in figure 6 and clearly illustrate the trend for facility of carbide formation. For the group V transition metals, the slopes remain constant and the carbide formation reaction becomes increasingly favourable (ΔG becomes negative) as the lines move from right to left, the order being determined as VC > NbC > TaC; this trend exactly mirrors that obtained experimentally for the dry reforming of methane over the group V metal carbides presented earlier. Increasing the temperature, for all the metal carbides, results in stabilisation of the system by lowering the Gibbs free energy of the recarbidation reaction, as was observed experimentally for the NbC catalyst system.

The thermodynamic calculations show that the Mo_2C, WC and VC materials should have a similar stability, since the temperature at which the Gibbs free energy for recarbidation becomes negative is similar for these three materials (i.e., 850–900 K). However, the group VI transition metals carbides and VC exhibit disparate catalytic behaviour. One reason for this may be differences in the carbide structure, since VC is fcc, while WC and Mo_2C are both hexagonal structures, as was shown in table 2. This structural difference may play a role in facilitating the recarbidation reaction or, in other words, may effect the kinetics of the oxidation and recarbidation reactions [16]. In addition, differences in electronic structure may be important and, indeed, it has been noted that the band structure of the group VI metal carbides more closely resembles that of the noble metals than is the case for the group V transition metals carbides [4,20,21].

Therefore, whilst the thermodynamic calculations have aided in the understanding of the stability order of the different carbides, it can only be used as a tool, since other factors are also important in determining the catalytic behaviour of these materials, probably effecting the reaction kinetics.

4. Conclusion

The group V and VI transition metal carbides were prepared and tested as catalysts for the industrially important methane dry reforming reaction. Mo_2C and WC were extremely stable, as has been reported previously [1], and may be potential alternatives to nickel catalysts in industrial processes. However, the group V metal carbides were much less stable, and their relative stabilities were predictable from Gibbs free energy calculations of the recarbidation reaction alone.

Acknowledgement

We are grateful to CANMET for funding this research, and AJB would like to thank the Rhodes Trust for a scholarship. We would also like to acknowledge Dr. G. Pez (Air Products plc.) for some helpful discussions.

References

[1] A.P.E. York, J.B. Claridge, A.J. Brungs, S.C. Tsang and M.L.H. Green, J. Chem. Soc. Chem. Commun. (1997) 39.

[2] G.A. Gazier, G.V. Samsonou, O.U. Kyloy, S.Z. Roginski, E.A. Forika and J.F. Yanouskii, Dokl. Akad. Nauk SSSR 140 (1961) 863.

[3] J.M. Muller and F.G. Gault, Bull. Soc. Chim. France 2 (1970) 416.

[4] R.B. Levy and M. Boudart, Science 181 (1973) 547.

[5] S.T. Oyama, in: *The Chemistry of the Transition Metal Carbides and Nitrides*, ed. S.T. Oyama (Blackie, Glasgow, 1996) ch. 1.

[6] R. Kapoor and S.T. Oyama, J. Solid State Chem. 99 (1992) 303.

[7] V.L.S. Teixeira da Silva, E.I. Ko, M. Schmal and S.T. Oyama, Chem. Mater. 7 (1995) 179.

[8] V.L.S. Teixeira da Silva, M. Schmal and S.T. Oyama, J. Solid State Chem. 123 (1996) 168.

[9] J.B. Claridge, A.J. Brungs and M.L.H. Green, Chem. Mater. (1998), submitted.

[10] L.G. Svintsova, V.V. Shimanovskaya, N.I. Il'chenko and G.I. Golodets, Kinet. Katal. 23 (1982) 398.

[11] J.-L. Dubois, K. Sayama and H. Arakawa, Chem. Lett. (1992) 5.

[12] J.G. Chen, J. Catal. 154 (1995) 80.

[13] L. Volpe and M. Boudart, J. Solid State Chem. 59 (1985) 332, 348.

[14] J.B. Claridge, M.L.H. Green, S.C. Tsang and A.P.E. York, Appl. Catal. 89 (1992) 103.

[15] E.K. Storms, *The Refractory Carbides*, Vol. 2 (Academic Press, New York, 1967).

[16] J.B. Claridge, A.P.E. York, A.J. Brungs, C. Márquez-Alvarez, J. Sloan, S.C. Tsang and M.L.H. Green, J. Catal., submitted.

[17] A. Erdöhelyi, J. Cserényi, E. Papp and F. Solymosi, Appl. Catal. 108 (1994) 205.

[18] V.C.H. Kroll, H.M. Swaan, S. Lacombe and C. Mirodatos, J. Catal. 167 (1997) 387.

[19] I. Barin, ed., *Thermodynamical Data of Pure Substances*, 2nd Ed. (VCH, Weinheim, 1993).

[20] M.E. Eberhart and J.M. Maclaren, in: *The Chemistry of the Transition Metal Carbides and Nitrides*, ed. S.T. Oyama (Blackie, Glasgow, 1996) ch. 5.

[21] A.F. Guillermet, J. Haglund and G. Grimwall, Phys. Rev. B 45 (1992) 11557.