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A new route to the metastable FCC molybdenum carbide α-MoC_{1-x}

Christophe Bouchy, Sharifah Bee Derouane-Abd Hamid* and Eric G. Derouane

Leverhulme Centre for Innovative Catalysis, Department of Chemistry, The University of Liverpool, Liverpool, UK L69 3BX. E-mail: sharifhd@liverpool.ac.uk

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The carburisation of a prereduced MoO_3 provides a new method for the synthesis of the metastable α-MoC_{1-x}.

Because of their potential as catalysts substituting noble metals, transition metal interstitial compounds,[1] especially carbides and nitrides of group VI (Mo, V, W),[2–5] have received considerable interest. Several routes have been proposed for their preparation and their catalytic properties have been evaluated for a variety of reactions.

The direct temperature programmed reduction (TPR) and carburisation of MoO_3 using methane allows the preparation of the thermodynamically stable β-phase of molybdenum carbide, β-Mo_2C, whose structure is hexagonal close packed (HCP), with specific surface areas in the range 50–100 $m^2\ g^{-1}$.[6] The metastable α-phase of molybdenum carbide, α-MoC_{1-x}, whose structure is face-centred cubic (FCC), possesses catalytic properties which differ from those of the β-phase as observed, for example, in the hydrogenolysis of ethane.[7] Two procedures have been proposed for its synthesis. The first one involves the initial reduction and nitridation of MoO_3 by ammonia followed by the carburisation of the γ-Mo_2N nitride.[8] The second consists in the direct reduction and carburisation of MoO_3 containing a small amount of platinum.[9] The first method is rather tedious whereas the second leads to α-MoC_{1-x} contaminated by platinum, which may affect its catalytic behaviour. We now report a new and direct route for the synthesis of α-MoC_{1-x} using pure MoO_3 as precursor.

The MoO_3 used was analytical grade and obtained from Aldrich. The structural transformations occuring during its reduction and carburisation were followed *in situ* using powder X-ray diffraction (XRD). A Paar XRD *in situ* cell, capable of operation up to *ca*. 900 °C and 10 bar, was mounted in a Siemens D5001 powder X-ray diffractometer (θ–2θ mode) equipped with a position sensitive detector enabling the fast (< 6 min) acquisition of detailed X-ray diffraction patterns.

The new synthesis route to α-MoC_{1-x} can be described as follows. MoO_3 is first reduced at 350 °C under pure dihydrogen flow for 24 h. *In situ* XRD characterisation showed (Fig. 1) that MoO_3 is converted by this reduction treatment into a mixture of the sub-oxide MoO_2 and of another phase previously identified as the oxyhydride MoO_xH_y.[10] The oxyhydride has an FCC structure with a_{cub} = 0.410 nm and is formed by reduction and hydrogen insertion in the MoO_3 lattice, the overall process being topotactic.[11]

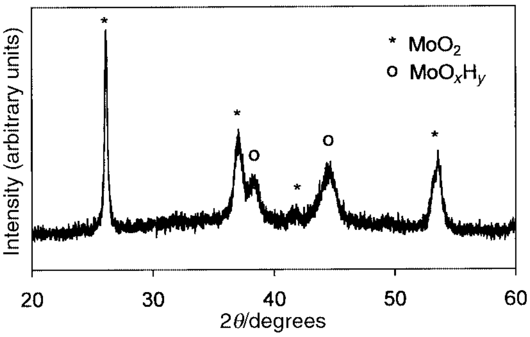

Fig. 1 *In situ* XRD pattern of the material obtained following reduction of MoO_3 by dihydrogen at 350 °C for 24 h.

Dihydrogen was then replaced by methane and the sample (mixture of MoO_2 and MoO_xH_y) heated progressively to 710 °C (3 °C min^{-1}). *In situ* fast scan XRD analyses were performed at regular 30 °C temperature intervals to follow the carburisation of the sample. As shown in Fig. 2, carburisation started at 620 °C and yielded eventually (680–710 °C) the nearly pure metastable carbide α-MoC_{1-x} with only traces of the stable carbide β-Mo_2C. The unit cell parameter (a_{cub}) of the FCC structure was found to be 0.428 nm, confirming that a pure carbide, and not an oxycarbide (lower a_{cub} values),[11,12] was synthesised. The particle size (coherent domain size) of α-MoC_{1-x}, calculated from the broadening of the XRD pattern, is *ca*. 3.4 nm, corresponding to an estimated surface area of 187 $m^2\ g^{-1}$. However, the specific surface area of the sample measured by the BET method was found to be much smaller (S_{BET} = 90 $m^2\ g^{-1}$), possibly because of the plugging of mesoporosity owing to carbon deposition on the sample during synthesis. The presence of carbon deposits was confirmed using the method of Lee *et al*.[6] and a C/$Mo_{surface}$ atomic ratio of 7 was found. The C_{bulk}/Mo_{bulk} atomic ratio of the sample was then estimated by *in situ* TPO of sample whose surface was coke-free, as a result of the former treatment. This ratio was found to be equal to 0.7 ± 0.1. The value of this ratio and of a_{cub} support the deduction that the carbide synthesised is similar to the FCC carbide previously reported in the literature.[13] An FCC carbide without coke contamination, *i.e.* directly usable for catalytic application, was synthesised by replacing the pure CH_4 gaseous flow by a H_2–CH_4 (9 : 1) mixture. In this case, S_{BET} was 179 $m^2\ g^{-1}$, with a pore size distribution centred around 3 nm. The formation of β-Mo_2C, in very small amount, is attributed to the

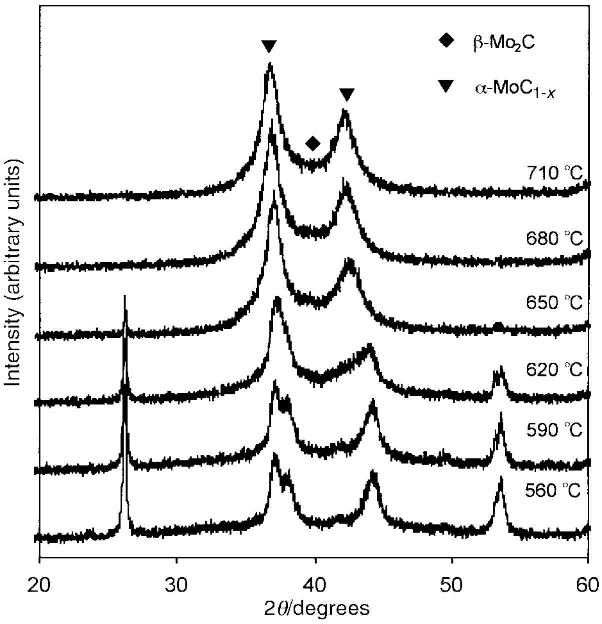

Fig. 2 *In situ* XRD characterisation of the MoO_2–MoO_xH_y mixture during methane carburisation.

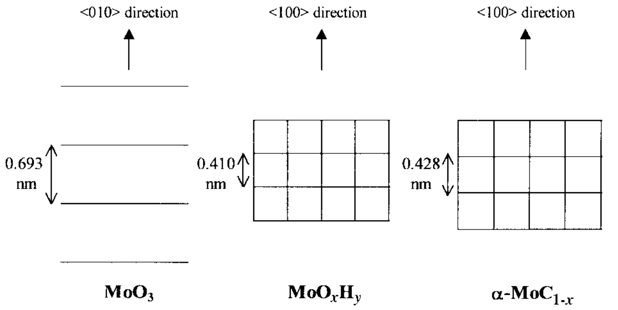

Fig. 3 Topotactic synthesis of FCC MoC_{1-x}: the < 010 > direction of the starting material is conserved during the synthesis.

carburisation of the MoO_2 sub-oxide as reported in the literature[14] whereas the carburisation of the oxyhydride MoO_xH_y yields α-MoC_{1-x}, both compounds having a FCC structure.

The synthesis of the FCC α-MoC_{1-x} carbide is enabled by the topotactic formation at low temperature of the FCC MoO_xH_y oxyhydride whose subsequent carburisation, occurring *via* a topotactic process,[11] leads to the FCC carbide. It appears that, as in the case of the topotactic synthesis of γ-Mo_2N from MoO_3,[15] the < 100 > direction of the FCC carbide is parallel to the < 010 > direction of the starting oxide (Fig. 3). The first step, *i.e.* the oxyhydride synthesis, is a further illustration of Figlarz's concepts about the usefulness of "soft chemistry"[16] when applied to the synthesis of new compounds in the MoO_3-WoO_3 system.

When compared to the two methods previously reported for the synthesis of α-MoC_{1-x}, the new route described above has two advantages. The first is its simplicity as no initial nitridation of MoO_3 with ammonia is required. The second is that the FCC carbide is obtained directly from pure MoO_3 and is thus not contaminated by traces of platinum.

These facts are certainly relevant if the α-MoC_{1-x} carbide is to be used as a catalyst, in order to avoid secondary reactions resulting from contamination by either γ-Mo_2N nitride (and its further reaction products) or platinum.

For example, it is known that bifunctional Mo-containing H-MFI zeolites, using $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ or MoO_3 as molybdenum sources, are efficient catalysts for the direct aromatisation of methane and that the active Mo-species in such systems is molybdenum carbide.[17,18] The new procedure proposed here for the preparation of α-MoC_{1-x} has enabled the quantitative evaluation and comparison of the performance of acidic zeolites modified by both the α- and β-phases of molybdenum carbide[19] without secondary effects owing to the presence of platinum impurities or to possible structural modifications of the zeolite or microporous solid following its prolonged exposure to ammonia at high temperature.[20]

In addition, as the carburisation of MoO_2 and MoO_xH_y leads to two different Mo-carbides, the treatment described above may be used to evidence the formation of the MoO_xH_y oxyhydride phase after a low temperature reductive treatment of MoO_3.[21,22]

In conclusion, a new simple and direct route has been found for the synthesis of the pure α-MoC_{1-x} carbide. This should enable a better quantification of its surface properties and reactivity and may impact on its use as catalyst for a variety of reactions.

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Notes and references

1 S. T. Oyama, *The Chemistry of Transition Metal Carbides and Nitrides*, Blackie Academic and Professional, London, 1996.

2 S. T. Oyama and G. L. Haller, *Surface and Defect Properties of Solids*, Specialist Periodical Reports, the Chemical Society, London, 1982, vol. 5, p. 332.

3 L. Leclerq, *Surface Properties and Catalysis by Non-metals*, ed. J. P. Bonnelle, D. Delmon and E. G. Derouane, Nato ASI Series, Washington DC, 1983, vol. 433.

4 M. J. Ledoux, C. Pham-Huu, J. Guille and H. Dunlop, *J. Catal.*, 1992, **134**, 383.

5 P. W. Lednor, *Catal. Today*, 1992, **15**, 243.

6 J. S. Lee, S. T. Oyama and M. Boudart, *J. Catal.*, 1987, **106**, 125.

7 G. S. Ranhotra, A. T. Bell and J. A. Reimer, *J. Catal.*, 1987, **108**, 40.

8 L. Volpe and M. Boudart, *J. Solid State Chem.*, 1985, **59**, 348.

9 J. S. Lee, L. Volpe, F. H. Ribeiro and M. Boudart, *J. Catal.*, 1988, **112**, 44.

10 P. Delporte, F. Meunier, C. Pham-Huu , P. Vennégues, M. J. Ledoux and J. Guille, *Catal. Today*, 1995, **23**, 251.

11 C. Bouchy, *PhD Thesis*, University Louis Pasteur, Strasbourg, 1998.

12 I. F. Ferguson, J. B. Ainscough, D. Morse and A. W. Miller, *Nature*, 1964, **202**, 1327.

13 E. Rudy, S. Windisch, A. J. Stosick and J. R. Hoffman, *Trans. TMS-AIME*, 1967, **239**, 1247.

14 S. T. Oyama, *Catal. Today*, 1992, **15**, 179.

15 L. Volpe, *PhD Thesis*, University of Stanford, 1985.

16 M. Figlarz, *Prog. Solid State Chem.*, 1989, **19**, 1.

17 F. Solymosi, A. Szoke and J. Cserenyi, *Catal. Lett.*, 1996, **39**, 157.

18 D. Wang, J. H. Lunsford and P. Rosynek, *J. Catal.*, 1997, **169**, 347.

19 S. B. Derouane-Abd Hamid, R. Anderson, I. Schmidt, C. Bouchy, K. Jacobsen and E. G. Derouane, oral presentation accepted at *APCAT 2000*, January, Australia *Catal. Today*, submitted.

20 E. Segal, I. Ivanova and E. G. Derouane, *Rev. Roum. Chim.*, 1993, **38**, 1127.

21 A. Katrib, V. Logie., P. Wehrer, L. Hilaire and G. Maire, *J. Chim. Phys.*, 1997, **94**, 1923.

22 T. Matsuda, H. Shiro, H. Sakagami and N. Takahashi, *Catal. Lett.*, 1997, **47**, 99.

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