Journal of Alloys and Compounds 473 (2009) L10–L12

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Letter

A new approach to the synthesis of molybdenum phosphide via internal oxidation and reduction route

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ARTICLE INFO

Article history:
Received 18 April 2008
Received in revised form 12 May 2008
Accepted 13 May 2008
Available online 26 June 2008

Keywords:
Inorganic materials
Chemical synthesis
Gas–solid reactions
Scanning electron microscopy
X-ray diffraction

ABSTRACT

A new method for the preparation of molybdenum phosphide was reported. Dispersed MoP with lamellar morphology was obtained from the decomposition of a mixed-salt precursor containing $(NH_4)_4Mo_7O_{24}{\cdot}2H_2O$, $(NH_4)_2HPO_4$ and hexamethylenetetramine under argon. During the thermal decomposition, reduction of molybdenum and phosphorous species by methane from the hexamethylenetetramine ligand occurred, with release of CO and CO_2. Compared with traditional H_2-temperature-programmed reduction method, the method developed provided a simple one-step way to molybdenum phosphide with relatively high surface area.

1. Introduction

Transition metal phosphides are currently of great interest in chemistry and materials sciences, because they exhibit various interesting properties, including superconductivity, magnetocaloric behavior, magnetoresistance and catalytic activity [1–5]. In particular, recent studies have shown that MoP and Ni_2P are synthesized from ammonium molybdate and ammonium phosphate by H_2-temperature-programmed reduction (TPR) method and show high activity for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) of petroleum feedstocks [6,7]. Unfortunately, the surface area of thus-prepared metal phosphides are very low, because the P—O bond is strong and its reduction requires high temperature. Therefore, it is important to develop simple synthetic approaches that yield bulk transition metal phosphides with higher surface areas. Despite, a variety of methods have emerged for the synthesis of these materials [8–12], the possibility of a range of preparative routes being available, very few others have been explored. Recently, Prins and co-workers reported that the bulk Ni_2P was synthesized via hydrogen reduction of the phosphate precursor in the presence of polymer surfactants and ethylene glycol [13]. In addition, Burns et al. reported the application of methane as a reductant in the preparation of bulk MoP [14]. Both binary metal phosphides were found to show relatively high surface areas, suggesting that the presence of carbon in metal phosphides was advantageous in preventing sintering of phosphides at high temperature.

In recent studies, the nitrides and carbides of transition metals can be obtained on the use of hexamethylenetetramine (HMT) as a reductant [15–18]. Based on the success with the HMT route to synthesize metal nitrides and carbides, we decided to examine whether this simple procedure can also be used to produce metal phosphides. In the present study, MoP was prepared in a one-step synthesis, in which a mixed-salt precursor containing $(NH_4)_4Mo_7O_{24}{\cdot}2H_2O$, $(NH_4)_2HPO_4$ and HMT was directly converted to phosphide under a flow of argon at 750 °C.

2. Experimental

An aqueous solution of $(NH_4)_4Mo_7O_{24}{\cdot}2H_2O$, $(NH_4)_2HPO_4$ and HMT was mixed with a mole ratio of 1:7:15; a few drops of $NH_3{\cdot}2H_2O$ were added in order to dissolve the precipitate. The solution was then evaporated slowly to dryness, and a white solid was obtained. After drying at 120 °C for 12 h, the solid was heated in a quartz reactor under a flow of argon (50 mL/min). The temperature was increased linearly at a rate of 10 °C/min and then kept at a given value for 2 h, followed by cooling to room temperature (RT) under argon flow, and then passivated at RT in a stream of $1\%O_2/He$. Three samples have been obtained from heating at 550, 650 and 750 °C, designated, respectively, as sample-550, sample-650 and sample-750.

X-ray diffraction (XRD) examination was carried out on a X-ray diffractometer (Rigaku D-Max Rotaflex) with Cu Kα radiation and Ni filter. Scanning electron microscopy (SEM) image was obtained using a KYKY 1000 B scanning electron microscope with an energy dispersive X-ray spectroscopic (EDS) system. The BET surface areas of passivated samples were measured on an ASAP 2010 instrument.

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doi:10.1016/j.jallcom.2008.05.048

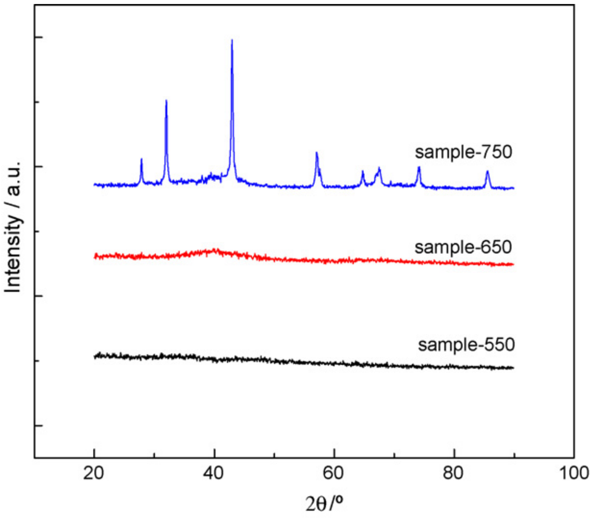

Fig. 1. XRD patterns of the products of mixed-salt precursor thermal decomposition in Ar flow at 550, 650 and 750 °C.

N_2 was used for standard five-point BET surface area measurements. The gases emitted during the decomposition were monitored using a mass spectrometer (MS, HP G1800A) and an infrared absorption spectrometer (IRAS, SICK-MAIHAK-S710). The signals of $m/e = 2$, 16, 17, 18, and 28 and the formation rates of CO, CO_2 and CH_4 in the gas phase effluent were continuously detected by MS and IRAS, respectively.

3. Results and discussion

The XRD patterns (Fig. 1) show that the sample-550 and sample-650 were completely amorphous, whereas the sample-750 demonstrated the formation of MoP crystalline phase. The lines at 27.9°, 32.0°, 42.9°, 57.0°, 64.7°, 67.4°, 74.0° and 85.5° corresponded to the ⟨0 0 1⟩, ⟨1 0 0⟩, ⟨1 0 1⟩, ⟨1 1 0⟩, ⟨1 1 1⟩, ⟨2 0 0⟩, ⟨2 0 1⟩ and ⟨1 1 2⟩ reflections of MoP, respectively. Subsequent BET analysis of this sample yielded a surface area of $10\,m^2\,g^{-1}$. Fig. 2 shows the SEM image and EDS result of the sample-750. Observation of Fig. 2a showed that the sample-750 consisted of submicrometer-sized thin sheets. The EDS results for the sample-750 are shown in Fig. 2b and give a P/Mo mole ratio of 0.95, which was a little lower than theoretical value. Wang et al. reported that, although the preparations were carried out with stoichiometric quantities of metal and phosphorus, the final products tended to be metal-rich due to the loss of phosphorus in the preparation processes [19].

Fig. 3a shows the MS of gaseous products from the decomposition of the mixed-salt precursor during linear heating in argon. Formation of gaseous products began 100 °C and was mostly completed at 800 °C. At low temperatures, the release of H_2O and NH_3 had coinciding maxima at 200 and 250 °C. Simultaneously, the formation of NH_3 decomposed via sequential dehydrogenation, giving H_2 and NH_x ($x = 0, 1, 2$). With increasing temperature, the detection of the intense H_2 signal at 530 °C was due to the decomposition of CH_4. Additionally, we observed a very weak signal of CH_4 ($m/e = 16$) at 750 °C, which coincided with the signals of H_2 ($m/e = 2$) and N_2 or CO ($m/e = 28$). As shown in Fig. 3b, the formation rates of CO, CO_2 and CH_4 in the outflow gas are determined by IRAS. The CO formation was observed with a weak peak at 300 °C, followed by the formation of large amount of CO and low levels of CO_2 at 750 °C. In addition, we detected the CH_4 formation with an intense peak at 260 °C but there was no obvious peak at 750 °C, possibly due to the detection limit for IRAS analysis of CH_4. The results suggested that the $m/e = 16$ signal below 500 °C in the mass spectra (Fig. 3a) was partly attributed to the product of CH_4, which could react with a portion of molybdenum and phosphorous species to give CO. During the decomposition, reduction of the last compound occurred with the simultaneous emission of CO and CO_2 at higher temperature. Form the results of XRD (Fig. 1), it can be observed that the minimum temperature (750 °C) at which the molybdenum phosphide was formed as the crystalline phase. Thus, it was reasonable to deduce that the internal oxidation and reduction process of the mixed-salt precursor was finally completed at 750 °C, which was in good agreement with the phenomena observed by MS and IRAS. It was worthy to note that the formation of CO and CO_2 certainly argued for oxidation of a carbonaceous species, but it was not possible to confirmative whether it was carbon or CH_4 from HMT decomposition. In view of point that the molybdenum and phosphorous species could be reduced to MoP by carbon, carbon-supported molybdenum phosphate with Mo loading of 30 wt.% and Mo/P ratio of 1/1 was prepared by pore-volume impregnation of a activated carbon support. The carbon-supported precursor was heated and passivated according to the procedure for the preparation of sample-750 to produce the carbon-supported sample. Subsequent XRD analysis (not shown) of this sample yielded a mixture of $MoOPO_4$ and MoO_2 phases on carbon support. The results inferred that the MoP could not be obtained from carbon-supported molybdenum phosphate precursor via carbothermal reduction method at a temperature of 750 °C. In other words, the molybdenum and phosphorous species were indeed reduced by CH_4 from the HMT ligand occurred, to give MoP phosphide with release of CO and CO_2.

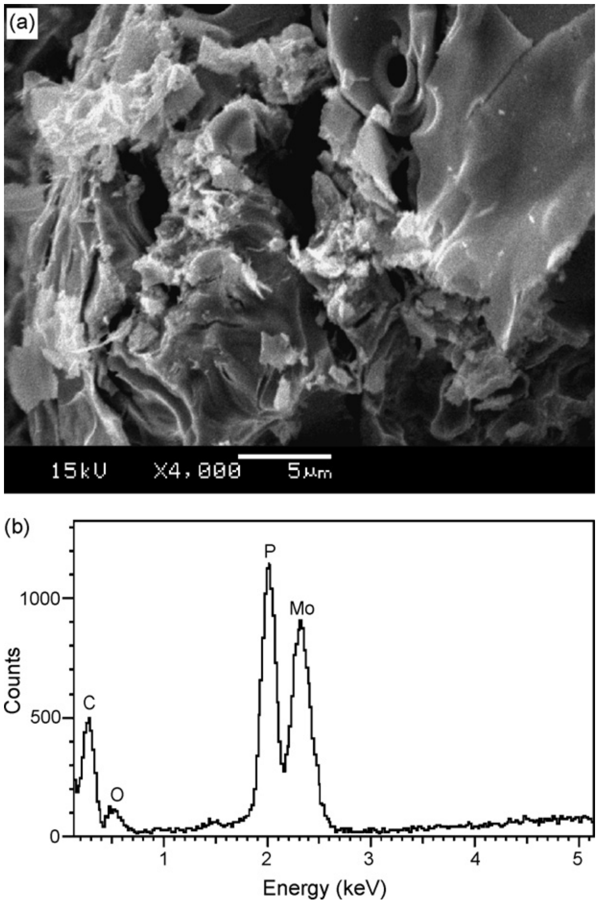

Fig. 2. (a) SEM image of MoP particle. (b) EDS result for the particle.

The ensemble of MS, IRAS and XRD analysis data allowed us to conclude that thermal decomposition of the mixed-salt precursor as an internal oxidation–reduction process in which methane reduced molybdenum and phosphorous species and was elimi-

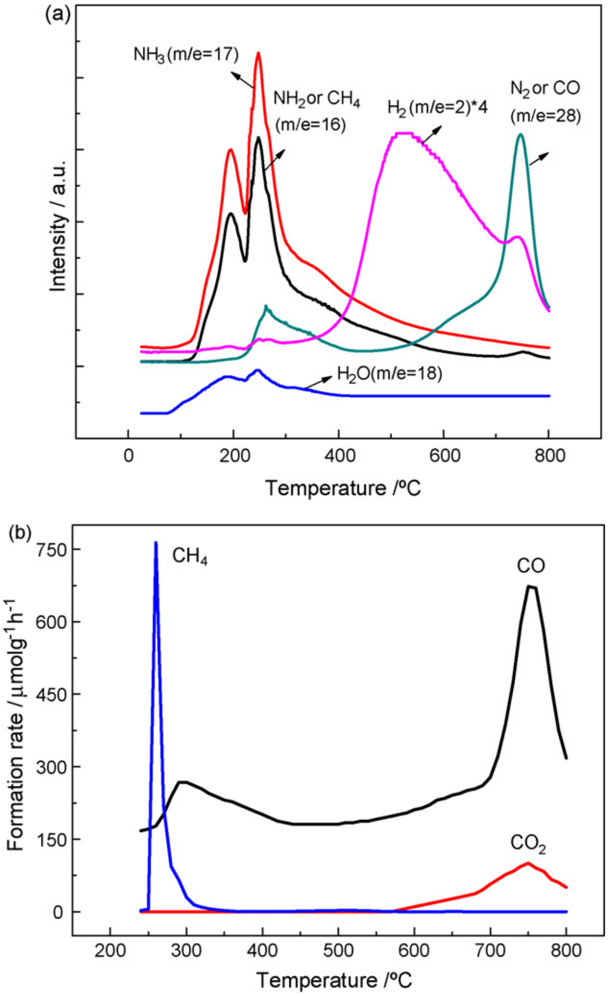

Fig. 3. Thermal decomposition of mixed-salt precursor at 10 °C/min followed by MS and IRAS.

nated as CO and CO_2. It was observed earlier that the intramolecular oxidation–reduction during the thermal decomposition of transition metals hexamethylenetetramine complexes can lead to the formation of metal carbides and nitrides [15–17].

The possible formation mechanism of molybdenum phosphide during the thermal decomposition process was proposed as follows: (1) HMT decomposed to CH_4, N_2 and C; (2) molybdenum and phosphorous species reacted with CH_4 to product the MoP particles and the gases of CO, CO_2 and H_2.

Traditional metal phosphide catalysts were prepared using the typical TPR method. The details were described elsewhere [20]. In the TPR method, the precursor was first calcined at 500 °C for 5 h and then reduced at a slow rate (1 °C/min) to 650 °C in a stream of hydrogen (300 mL/min), whereas in this new method, the precursor was directly heated at a rate of 10 °C/min to 750 °C under argon with a flow rate of 50 mL/min. Comparison of the two syntheses clearly indicated that the new method described here was simpler and more straightforward. Furthermore, the BET surface area of 10 $m^2 g^{-1}$ for the material prepared by this new method was larger than the value of 2 $m^2 g^{-1}$ for that prepared by TPR method [20]. It was reported that a large amount of water produced in TPR process, which can lead to hydrothermal sintering and low surface area of the resulting catalysts [14]. On the contrary, in the present synthesis route, it was apparent that CO and CO_2 were the major products, and no quantification of H_2O was made overall reduction process. This was a point worthy of which suggested the use of CH_4 as reductant in phosphide synthesis procedure can adapt to minimize hydrothermal sintering. Additionally, it was reasonable to believe that a degree of carbon lay-down arised from HMT route to MoP, and the presence of carbon in the metal phosphides was reported to be advantageous in preventing high temperature sintering of phosphide particles [13,14]. Therefore, the content of HMT in the precursor had an influence on the products and should be carefully optimized. The internal oxidation–reduction synthesis route is expected to be a general method for the generation of relatively high surface area phosphides.

4. Conclusion

A new one-step method was found for the synthesis of MoP. Decomposition of the mixed-salt precursor provided a synthesis route free of diffusion limitations. Such a simple and straightforward synthesis route in this paper, suggests that it may be possible to further optimize the synthesis described for the production of high surface area phosphides.

Acknowledgements

The work was supported by the National Natural Science Foundation of China (No. 20573014) and the Natural Science Foundation of Liao-Ning Province (20041072).

References

[1] L.E. DeLong, G.P. Meisner, Solid State Commun. 53 (1985) 119–123.
[2] O. Tegus, E. Brück, K.H.J. Buschow, F.R. de Boer, Nature 415 (2002) 150–152.
[3] S.T. Oyama, J. Catal. 216 (2003) 343–352.
[4] J. Jiang, S.M. Kauzlarich, Chem. Mater. 18 (2006) 435–441.
[5] D.C.S. Souza, V. Pralong, A.J. Jacobson, L.F. Nazar, Science 296 (2002) 2012–2015.
[6] S. Yang, R. Prins, Chem. Commun. (2005) 4178–4180.
[7] C. Stinner, R. Prins, Th. Weber, J. Catal. 191 (2000) 438–444.
[8] K.A. Gregg, S.C. Perera, G. Lawes, S. Shinozaki, S.L. Brock, Chem. Mater. 18 (2006) 879–886.
[9] K.L. Stamm, S.L. Brock, J. Alloys Compd. 453 (2008) 476–481.
[10] Y. Xie, H.L. Su, X.F. Qian, X.M. Liu, Y.T. Qian, J. Solid State Chem. 149 (2000) 88–91.
[11] C.M. Lukehart, S.B. Milne, S.R. Stock, Chem. Mater. 18 (1998) 903–908.
[12] K.L. Stamm, J.C. Garno, G. Liu, S.L. Brock, J. Am. Chem. Soc. 125 (2003) 4038–4039.
[13] S. Yang, C. Liang, R. Prins, J. Catal. 241 (2006) 465–469.
[14] S. Burns, J.S.J. Hargreaves, S.M. Hunter, Catal. Commun. 8 (2007) 931–935.
[15] P. Afanasiev, Inorg. Chem. 41 (2002) 5317–5319.
[16] H. Wang, W. Li, M. Zhang, Chem. Mater. 17 (2005) 3262–3267.
[17] S. Chouzier, P. Afanasiev, M. Vrinat, T. Cseri, M. Roy-Auberger, J. Solid State Chem. 179 (2006) 3314–3323.
[18] N. Fan, X. Ma, Z. Ju, J. Li, Mater. Res. Bull. 43 (2008) 1549–1554.
[19] X. Wang, P. Clark, S.T. Oyama, J. Catal. 208 (2002) 321–331.
[20] C. Stinner, R. Prins, Th. Weber, J. Catal. 202 (2001) 187–194.