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Synthesis of Bulk and Supported Molybdenum Carbide by a Single-Step Thermal Carburization Method

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A facile and effective method for the preparation of bulk and alumina-supported molybdenum carbide is described. The synthesis of molybdenum carbide β-Mo_2C has been conducted by a single-step heat treatment of a mixed salt precursor containing molybdenum HMT (HMT = hexamethylenetetramine) complex and HMT in argon atmosphere up to 700 °C. The formation process of the carbide has been investigated. Alumina-supported nanocrystalline β-Mo_2C has also been successfully prepared with this method. The resultant catalyst exhibits good hydrodesulfurization (HDS) activity. It indicates that this simple method is an effective way to synthesize active carbide catalysts.

Introduction

Transition-metal carbides have received considerable attention as advanced materials in recent years for their attractive physical and chemical properties including mechanical hardness, thermal stability, superconductivity, and especially in catalytic performance.[1,2] In particular, the metal carbides as catalytic materials have been found to show excellent activity for certain reactions, which are similar to that of noble metal catalysts.[3] One of the most actively studied systems is molybdenum carbide, which is proved to be an attractive catalyst for methane reforming,[4−6] ammonia synthesis and decomposition,[7,8] aromatization,[9,10] hydrazine decomposition,[11] hydrogenation,[12] and hydrodesulfurization (HDS).[13−16]

The traditional methods for the synthesis of metal carbide involved direct carburization of metals with graphitic carbon at high temperature, for example, >1000 °C for Mo_2C, and were unsuitable to catalytic application because of the very low surface area of the products. Since the 1980s, a temperature-programmed reduction (TPRe) method was established[17] and widely used to prepare transition-metal nitride and carbide with large surface area. It induced the solid-state transformation of oxides in a controlled manner by reacting with a mixture of hydrogen and carbon-containing gases such as CH_4,[17−20] C_2H_6,[21−23] C_3H_8,[24] C_4H_{10},[25,26] and CO.[20,27] The TPRe method was proved to be an effective and general way to prepare active catalysts. However, the synthesis conditions were quite complex and rigid, which influence the catalytic properties of the carbide materials, and the resultant carbide surface was usually contaminated by polymeric carbon generated from the pyrolysis of the carbon-containing gases. The development of new methods such as gas-phase reactions of volatile metal compounds,[28] pyrolysis of metal complexes,[29,30] solid-state metathesis

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(SSM) reactions,[31] and solid−solid carburization of metallic compounds[32−37] has gained increasing attention in recent years.

In this regard, one of the most intensive and promising methods was direct thermal solid−solid carburization of metal compounds with carbon or carbon-containing materials from designed precursors. Shin et al.[32] reported the use of cellulose as carbon precursor and aqueous-based Tyzor-LA as TiO_2 source for the synthesis of TiC nanoparticles by carbonthermal reduction in argon atmosphere. Ganesan and Lee[33] have synthesized W_2C microspheres by heating mixtures of resorcinol−formaldehyde polymer as carbon precursor and ammonium metatungstate salt as tungsten precursor. Shanmugam et al.[34] have reported a single-step synthesis of WC by direct pyrolysis of a hybrid composite at 1000 °C. Liang and co-workers[35−37] have prepared nanostructured Mo_2C, W_2C, and bimetallic CoMo carbide using ultrahigh-surface-area carbon material as carbon source in carbothermal hydrogen reduction. When compared with the TPRe method, these solid−solid carburization methods are simple, do no require high flow rate gas hydrocarbons, and no slow ramp rate is required. However, these methods have difficulties to prepare supported carbide catalysts or can only be used to get carbon material supported carbide catalysts.

In this study, we have put forward a simple solid−solid carburization method for the synthesis of both bulk and supported β-Mo_2C catalyst. The synthesis of molybdenum carbide has been conducted by a simple heat treatment of a mixed salt precursor in argon atmosphere up to 700 °C. This new method was based on the hexamethylenetetramine (HMT) method, which involved the formation of γ-Mo_2N from decomposition of a molybdenum HMT complex. The method was proved to be an effective way to prepare mono- and bimetallic molybdenum nitride.[38,39] Herein, the mixture of molybdenum HMT complex with HMT was used as precursor. The subsequent treatment at 700 °C in argon atmosphere led to the formation of hexagonal closed packed (hcp) β-Mo_2C. Obtaining a catalyst with large surface area, alumina-supported β-Mo_2C has also been successfully prepared using this simple method. Their catalytic activity was evaluated using HDS reaction and the resultant catalyst exhibits good HDS activity.

Experimental Sections

Synthesis. *Synthesis of Bulk β-Mo_2C.* All reagents used were of analytical purity. The precursors, which was the mixture of $(NH_4)_4(HMT)_2Mo_7O_{24}{\bullet}4H_2O$ (Mo−HMT) and HMT, could be prepared from two routes: mechanically mixing the two solids or evaporating an aqueous solution of $(NH_4)_6Mo_7O_{24}{\bullet}4H_2O$ (AHM) and HMT. To get supported carbide by impregnation method, the latter route was used. The precursor was prepared by dissolving $(NH_4)_6Mo_7O_{24}{\bullet}4H_2O$ and HMT with desired mole ratio in 15% $NH_3{\bullet}H_2O$ solution. The solution was evaporated slowly to dehydrate and was dried in vacuum at 80 °C for 3 h. A white solid was obtained as the precursors, which is the mixture of Mo−HMT and HMT. The solid was then heated in a stainless steel boat under a flow of argon (99.99%). The temperature was increased linearly at a rate of 15 °C min^{-1} and then was kept at a given temperature for 2 h. The product was cooled to room temperature (ca. 5 °C min^{-1}) under argon and was passivated in a flow of 1% (v/v) O_2/N_2.

To investigate the formation process, some intermediate samples were prepared. The precursor was heated to the desired temperature and then was cooled rapidly (ca. 100 °C min^{-1}) to room temperature. After cooling, the products were passivated as described above.

Synthesis of Alumina-Supported β-Mo_2C. The alumina-supported mixed salt precursor was prepared by impregnation of γ-Al_2O_3 with an aqueous solution of $(NH_4)_6Mo_7O_{24}{\bullet}4H_2O$ and HMT with a fixed mole ratio 1:9, which was obtained by dissolving the reagents in 15% $NH_3{\bullet}H_2O$ solution. The sample was then dried naturally for 48 h and was dried in vacuum at 80 °C for 3 h. The precursor was heated at a rate of 15 °C min^{-1} and was kept at 700 °C for 2 h under a flow of argon. The sample was cooled and passivated as described previously to obtain the supported carbide. The β-Mo_2C/γ-Al_2O_3 catalysts with theoretical loadings of 15, 23, 28, and 40 wt % β-Mo_2C were prepared. To evaluate catalytic activity, the precursor was pressed under 20.0 MPa and was smashed to 20−40 mesh particles prior to heat treatment.

Characterization. X-ray diffraction (XRD) characterization was conducted using a Rigaku D/max-2500 powder diffractometer employing Cu Kα radiation (40 kV, 40 mA). Transmission electron microscopy (TEM) images were acquired using a TECNAI G2 T20 high-resolution transmission electron microscope equipped with an Energy Dispersive X-ray spectrometer (EDX) system (EDAX) operating at 200 kV. The samples were dispersed in ethanol and were treated with ultrasound for 5 min and then were placed on a copper grid coated with holey carbon. The EDX signals of the nitride particles were obtained by focusing the electron beam on the particles and accumulating the spectra. Scanning electron microscopy (SEM) images were obtained using a LEO 1530VP scanning electron microscope. Single-point Brohaver Emmett Teller (BET) surface area and pore volume measurements employing nitrogen adsorption were acquired using a Micromeritics ASAP 2010 apparatus. The carbon, nitrogen, and hydrogen analyses of the samples were carried out with an Elementar Vario EL elemental analyzer.

Catalytic Activity Test. The catalytic activity of the HDS of dibenzothiophene (DBT, 0.5 wt %) was determined using a fixed-bed continuous-flow microreactor. The 1.2 g (∼2.0 mL) of the catalyst was diluted with SiO_2 to a volume of 5.0 mL in the reactor. Prior to reaction, the catalyst was pretreated in situ with flowing H_2 (30 mL/min) at 400 °C for 3 h. The reactions were carried out using the following experimental conditions: temperature = 280, 300, and 320 °C, feed rate = 10.0 mL h^{-1}, H_2 pressure = 3.0 MPa, and H_2 flow rate = 200 mL min^{-1}. In all cases, the liquid samples were collected at a 1-h interval after a stabilization period of 5 h and were analyzed by gas chromatography. For comparison purpose, the catalytic activities of a β-Mo_2C/γ-Al_2O_3 catalyst and two γ-Mo_2N/γ-Al_2O_3 catalysts were also evaluated. (The preparation of these catalysts was described in the Supporting Information.)

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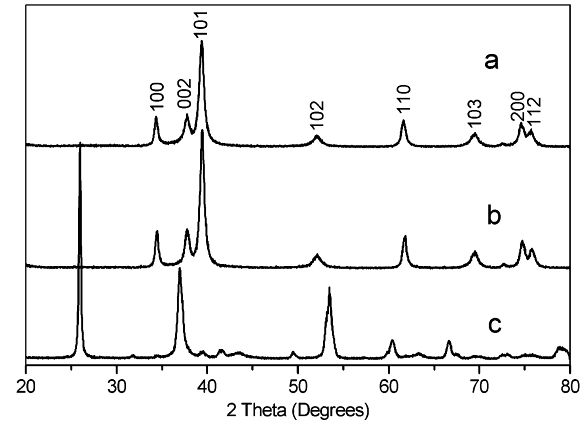

Figure 1. The XRD patterns of the samples prepared from different precursors: (a) the mixture of Mo−HMT and HMT obtained from evaporation of the solution, (b) the mixture of Mo−HMT and HMT by mechanical mixing of the two species, and (c) the mixture of AHM and HMT by mechanically mixing of the two species.

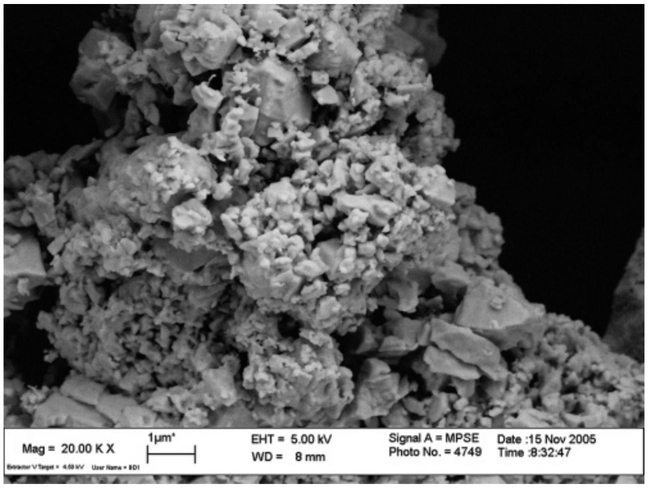

Figure 2. The SEM image of the as-prepared bulk β-Mo_2C.

Results and Discussion

Synthesis of Bulk Molybdenum Carbide. As shown in Figure 1 a, the bulk β-Mo_2C was successfully prepared by a single-step synthesis from the mixed-salt precursor, in which the precursor with Mo−HMT and HMT mole ratio of 1:7 was treated at 700 °C for 2 h with the ramp rate of 15 °C min^{-1} in flowing argon. Typical diffraction peaks of β-Mo_2C show clearly at 39.4°, 37.8°, 34.4°, 61.6°, 74.6°, 75.7°, 69.5°, and 52.0°, and no other peaks according to molybdenum oxides or nitrides appear. It indicates that the obtained β-Mo_2C is single phase to XRD. The carbon content in bulk sample is 5.60 wt %, which is consistent with the calculated value (5.89 wt %) and proves that no excess carbon exists. However, the sample contains minor nitrogen (0.33 wt %), which can be attributed to the existence of decomposition residue, minor molybdenum nitride, or nitricarbide that is below the detection limit for XRD. The SEM image of the product is given in Figure 2. The morphology of the bulk β-Mo_2C shows nucleated irregularly shaped particles with various sizes. The BET surface area of as-prepared β-Mo_2C has been measured to be 31.9 m^2 g^{-1}.

As discussed later, the carbide is formed at adequately high temperature by the carburization of γ-Mo_2N from decomposition of the complex with the carbon-enriched pyrolysate from decomposition of HMT. It means that the formation of the complex in the precursor, the HMT content in the precursor, and the reaction temperature are the key factors. Hereby, a series of precursors prepared by different routes, or with different Mo−HMT and HMT molar ratios, waere prepared and treated at varying temperatures. The elemental analyses' and XRD patterns of the products are listed in Table 1 and are given in Figure 1, Figure 3, and Figure 4.

Influence of the Preparation of the Precursor. To understand the composition of the precursor, three routes were first carried out to prepare different precursors: (a) the mixture of Mo−HMT and HMT at molar ratio of 1:7 obtained from evaporation of the solution, (b) the mixture of Mo−HMT (obtained using the method shown in the literature[38]) and HMT at molar ratio of 1:7 by mechanically mixing the two species, and (c) the mixture of AHM and HMT at molar ratio of 1:9 by mechanically mixing the two species. The three precursors were treated at 700 °C for 2 h with the ramp rate of 15 °C min^{-1} in flowing argon. The XRD patterns of the obtained products are given in Figure 1. The figure clearly shows that treatment of the precursors obtained through routes a and b can give bulk β-Mo_2C, whereas that through route c leads to MoO_2. The results indicate that the formation of Mo−HMT complex in the precursor is a necessary condition for preparing molybdenum carbide and that the precursor is a fine mixture of Mo−HMT and HMT. In addition, the results show that the preparation of precursor in this method is very simple and facile, which does not need special synthesis techniques. To get supported carbide by impregnation method, the solution route (route a) is used in the subsequent experiments.

Influence of the Mo−HMT and HMT Mole Ratio in the Precursor on the Products. To investigate the influence of HMT content, a series of precursors with different Mo−HMT and HMT mole ratios was prepared and treated at 700 °C for 2 h with the ramp rate of 15 °C min^{-1} in flowing argon. When there is no excessive HMT in existence, the Mo−HMT decomposes to get γ-Mo_2N (Figure 3a), which is in good agreement with the results reported by others.[39] Increasing the HMT content in the precursor, in which the mole ratio of Mo−HMT and HMT is 1:2, brings on the formation of β-Mo_2C with the presence of γ-Mo_2N (Figure 3b). The elemental analyses show the existence of both carbon and nitrogen. As the HMT content increases to make the mole ratio of Mo−HMT and HMT reach 1:7 in the precursor, the nearly single-phase β-Mo_2C is obtained. With continuous increasing of the HMT content, there is not any change in the XRD patterns and the β-Mo_2C is still the only products. The content of carbon is also consistent with the theoretical value and only carbon in carbide existed. As mentioned later, the excessive carbon-enriched pyrolysate of HMT can completely decompose, and thus there is no residuary carbon in existence in the resultant carbide. The results indicate that the abundant HMT in the precursor, which is used as carbon source, is necessary for the formation of single-phase carbide.

Influence of the Reaction Temperature on the Products. The precursor with Mo−HMT and HMT mole ratio of 1:7

Table 1. Phase Identification and Carbon and Nitrogen Content of the Products

mole ratio[a]	reaction temperature (°C)	phase identification[b]	carbon (wt %)	nitrogen (wt %)
1:7	700	Mo_2C (Figure 1a, 3c, 4d)	5.60	0.33
1:7	700	Mo_2C (Figure 1b)	5.67	0.39
1:9[c]	700	MoO_2 (Figure 1c)		
∞[d]	700	Mo_2N (Figure 3a)	0.07	6.73
1:2	700	Mo_2C Mo_2N (Figure 3b)	3.13	3.75
1:13	700	Mo_2C (Figure 3d)	5.82	0.28
1:7	680	Mo_2C Mo_2N (Figure 4c)	4.22	2.82
1:7	650	Mo_2C Mo_2N (Figure 4b)	3.84	3.68
1:7	600	Mo_2N (Figure 4a)	6.73	4.30

[a] The mole ratio of Mo−HMT and HMT in the precursor. [b] Obtained from XRD results. [c] The mole ratio of AHM and HMT in the precursor. [d] Single-phase Mo−HMT.

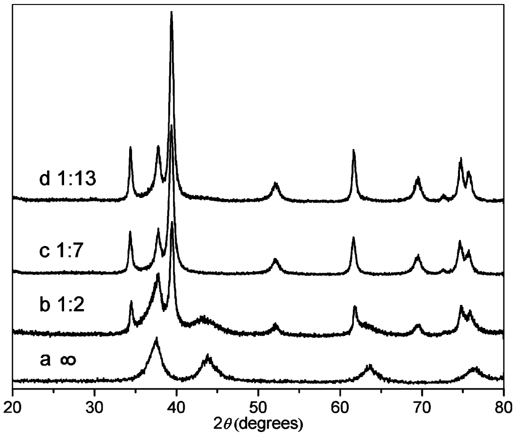

Figure 3. The XRD patterns of the samples prepared from the precursors with different Mo−HMT and HMT mol ratios: (a) ∞, (b) 1:2, (c) 1:7, and (d) 1:13.

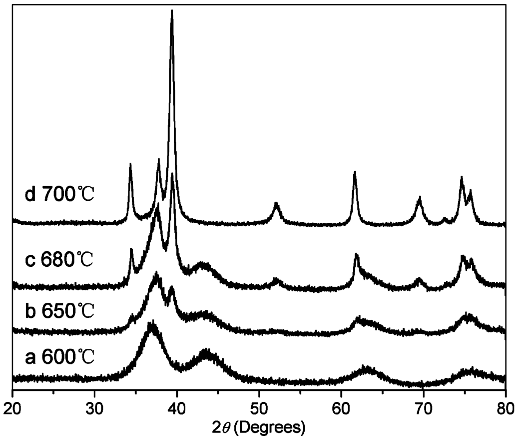

Figure 4. The XRD patterns of the samples prepared at different temperatures: (a) 600 °C, (b) 650 °C, (c) 680 °C, and (d) 700 °C.

was processed at different temperatures. As shown in Figure 4, the XRD patterns of the sample produced at 600 °C shows broad reflections that are characteristic of face-centered cubic (fcc) γ-Mo_2N structure. When the reaction temperature increases to 650 °C, the β-Mo_2C can be found with the existence of γ-Mo_2N. After treating at 680 °C for 2 h, the intensity of the detectable peaks of the carbide in the product pattern is enhanced and the peaks of the nitride exist. Although the holding time of heat treatment at 680 °C was extended to 4 h, the mixture of carbide and nitride was still obtained (XRD pattern is not given). When the precursor was heated at 700 °C for 2 h, the sharp peaks of β-Mo_2C were observed in the XRD pattern and single-phase carbide was obtained. It indicates that an elevated temperature ($\geq$700 °C) is a necessary condition for obtaining bulk β-Mo_2C in this method.

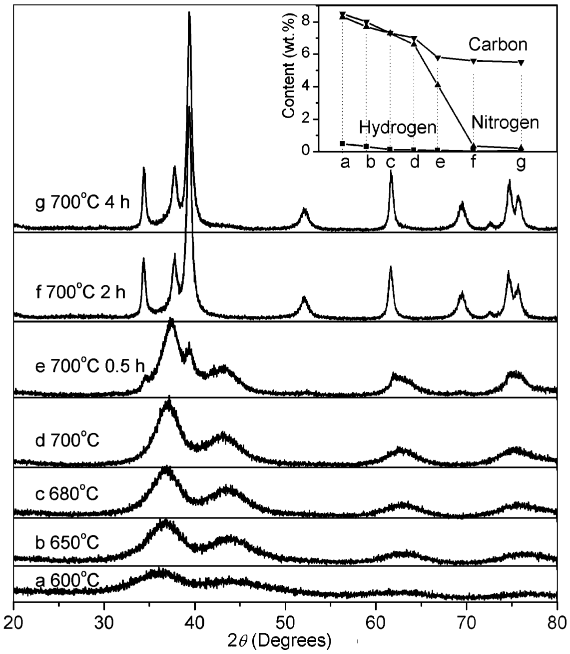

Figure 5. The XRD patterns and carbon, nitrogen, and hydrogen contents (as the curves show in inset) of the intermediate samples in the preparation of the bulk β-Mo_2C.

The above experiments clearly indicate that the key preparation conditions of the bulk β-Mo_2C by this method are as follows: a finely mixed Mo−HMT and HMT as precursor, sufficient HMT as carbon source in the precursor (Mo−HMT:HMT = 1:7), and heat treatment of the precursor in the argon atmosphere at an elevated temperature ($\geq$700 °C) and with enough holding time (2 h). This new synthesis route has some obvious advantages: (1) the starting materials are inexpensive, (2) the preparation process is simple and facile, (3) no high flow rate gas hydrocarbons and no slow ramp rate are required, and (4) the aqueous solution-based process is very helpful to prepare supported carbide catalysts. It shows that this method is a potential route for the production of β-Mo_2C in large scale.

Investigation of the Formation Process. To investigate the formation process of the molybdenum carbides, some intermediate samples were obtained and characterized. Figure 5 shows a series of XRD patterns of the intermediate samples at different temperatures, in which the inset is the curve of carbon, nitrogen, and hydrogen contents. It can be seen that the Mo−HMT in the precursor was decomposed to give γ-Mo_2N and that the abundant HMT was transformed into some pyrolysate at 600 °C. When the temperature increased from 600 °C to 700 °C, γ-Mo_2N and pyrolysate still continued to exist. At the same time, the contents of carbon, nitrogen, and hydrogen slowly decreased, which suggests that the pyrolysate continued to decompose. When the temperature reached 700 °C, the content of the nitrogen in the sample was 6.6 wt %, which accorded with the theoretical value of γ-Mo_2N, and 7.0 wt % carbon and a small quantity of hydrogen existed. It proved that γ-Mo_2N and carbon-enriched pyrolysate exist. The content of carbon was a little larger than the theoretical content of β-Mo_2C, and the carbon was sufficient for the replacement of nitrogen in the γ-Mo_2N to get β-Mo_2C. As expected, the replacement took place when the temperature was kept at 700 °C. As the holding time increased, the content of nitrogen quickly decreased while the content of carbon slightly changed, indicating that the nitrogen in γ-Mo_2N was replaced by the carbon. The XRD patterns also confirmed that the γ-Mo_2N was transformed into β-Mo_2C in this procedure. When the sample was heated at 700 °C for 2 h, the carburization completed and the desired product β-Mo_2C was obtained as nearly a single phase. The content of carbon in the sample slightly decreased on remaining at 700 °C and finally approached the theoretical content of β-Mo_2C, which indicated that the excessive carbon-enriched pyrolysate could completely decompose, and thus almost no residuary carbon existed in the resultant carbide. Further treatment at 700 °C for 4 h did not produce an obvious change in XRD, while the content of nitrogen slightly decreased, indicating that the carburization was still running.

The results reveal that the β-Mo_2C is formed by the carburization of γ-Mo_2N from decomposition of Mo−HMT with the carbon-enriched pyrolysate from decomposition of HMT on remaining at 700 °C. From the above experiments, we can clearly describe the formation process of β-Mo_2C as follows: the precursor is a fine mixture of Mo−HMT and HMT, in which Mo−HMT is the molybdenum source and the sufficient HMT is the carbon source. When the precursor is treated in argon at temperature below 700 °C, the Mo−HMT is decomposed to form γ-Mo_2N while the HMT is decomposed to give carbon-enriched pyrolysate (C*).

$$(NH_4)_4(HMT)_2Mo_7O_{24}\cdot 4H_2O \rightarrow \text{decomposition} \rightarrow \gamma\text{-}Mo_2N \quad HMT \rightarrow \text{decompostion} \rightarrow C^* \qquad (1)$$

A mixture of γ-Mo_2N and C* is obtained when the temperature reached 700 °C. When the temperature is held at 700 °C, the carburization reaction occurs.

$$\gamma\text{-}Mo_2N + C^* \rightarrow \text{carburization} \rightarrow \beta\text{-}Mo_2C \qquad (2)$$

In this stage, carbon replaces the nitrogen in nitride, the arrangement of Mo atom is changed from fcc (face-centered cubic) to hcp (hexagonal closed packed), and the β-Mo_2C is formed by the solid−solid carburization reaction between γ-Mo_2N and C*.

It is obvious that this new method is similar to the existing solid−solid carburization methods,[32−37] in which the carbides are synthesized by thermal solid−solid carburization of metal compounds with carbon or carbon-containing materials from finely designed precursors. However, there are no reports on the solid−solid carburization reaction between metal nitride and carbon or carbon-containing materials. As mentioned previously, all of the metal sources used in the existing solid−solid carburization methods are metals or metal oxides. In addition, it is notable that the carburization of γ-Mo_2N by gas hydrocarbons such as CH_4/H_2 in TPRe method gives metastable fcc α-MoC_{1-x}, in which the transformation of γ-Mo_2N to α-MoC_{1-x} follows a topotactic route.[8,40] However, in our study, the solid−solid carburization reaction of γ-Mo_2N with carbon-containing materials forms stable hcp β-Mo_2C. It proves that the transformation of nitride to carbide in this solid−solid reaction is a nontopotactic route, while the arrangement of Mo atom is changed in this procedure.

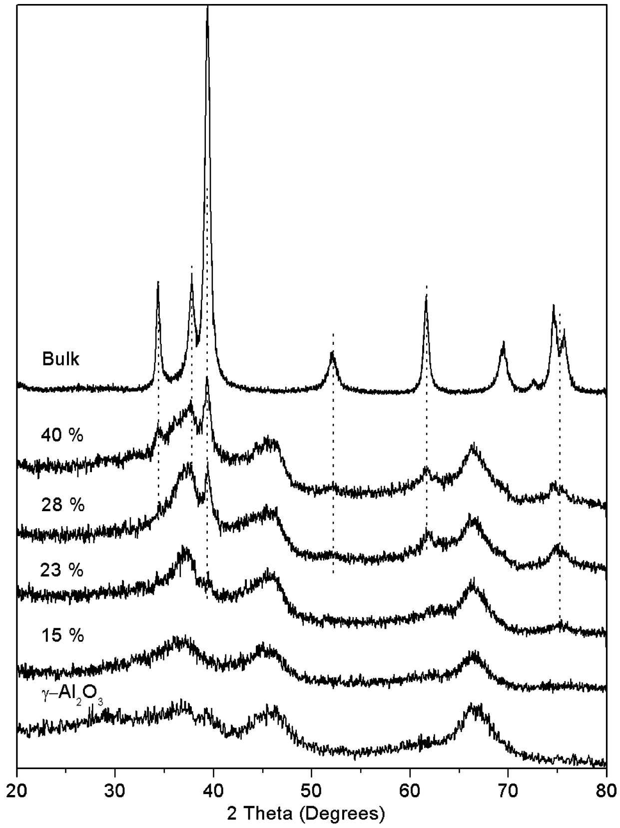

Figure 6. XRD patterns of the β-Mo_2C/γ-Al_2O_3 catalysts with theoretical loadings of 15, 23, 28, and 40 wt %. Also shown for comparison purpose are the XRD patterns for γ-Al_2O_3 and bulk β-Mo_2C.

Synthesis of Alumina-Supported β-Mo_2C and Its HDS Activity. The success of this synthesis method for bulk β-Mo_2C led us to consider its applicability for the preparation of supported carbide used as high surface area catalysts or bifunctional catalysts.

As shown in Figure 6, a series of β-Mo_2C/γ-Al_2O_3 catalysts (15−40 wt % Mo_2C) have been successfully prepared by treating alumina-supported mixed salt precursors at 700 °C for 2 h in flowing argon. No obvious XRD peaks associated with β-Mo_2C are apparent above the patterns of γ-Al_2O_3 for loadings below 23 wt % because of the small

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[40] Jung, K. T.; Kim, W. B.; Rhee, C. H.; Lee, J. S. *Chem. Mater.* **2004**, *16*, 307.

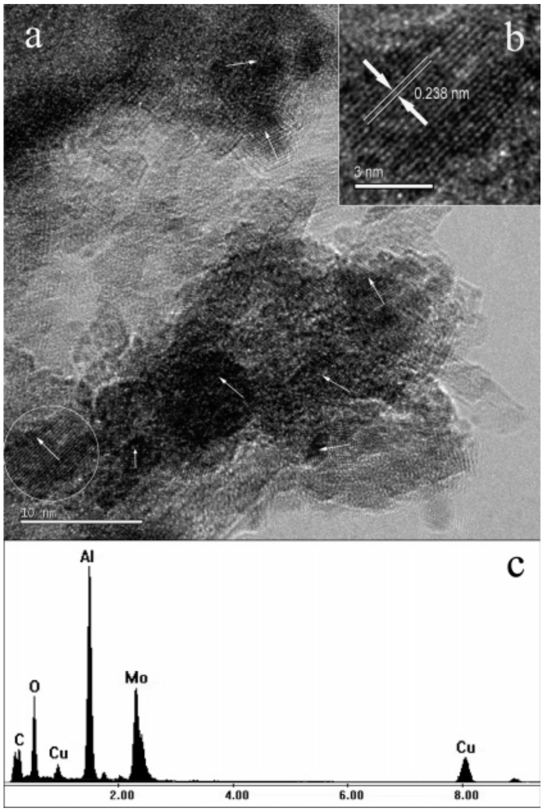

Figure 7. The as-prepared 23 wt % β-Mo_2C/γ-Al_2O_3 material: (a) TEM micrograph, (b) an enlarged image of a β-Mo_2C particle, and (c) EDX result of the area.

crystallite size of β-Mo_2C on the support which is below the detection limit for XRD. When the loading of the carbide increases to 28 wt % and 40 wt %, the XRD patterns show some additional peaks located at ~39.4°, ~37.8°, and ~34.4°, which are all in accord with those of β-Mo_2C. It indicates that the alumina-supported β-Mo_2C can be prepared in a wide range of β-Mo_2C loadings and crystallite sizes with this method. The BET surface area and pore volume of as-prepared 23 wt % β-Mo_2C/γ-Al_2O_3 has been measured to be 201.2 m^2 g^{-1} and 0.51 cm^3 g^{-1}, respectively. The TEM image and EDX results of the as-prepared 23 wt % β-Mo_2C/γ-Al_2O_3 are given in Figure 7. The EDX results prove the existence of Mo element in the area. Observation of Figure 7a shows fairly uniform nanoparticles with the size of 3−8 nm, indicating a good dispersion on the support. An enlarged image of a particle (Figure 6b), as well as others, yields *d* spacing value of 0.238 nm for the {121} crystallographic plane of β-Mo_2C, which is in good agreement with the calculated value. It proves the formation and good dispersion of nanocrystalline β-Mo_2C on the support.

Table 2. Catalytic Activity of the As-Prepared 23 wt % β-Mo_2C/γ-Al_2O_3 Catalysts and 23 wt % γ-Mo_2N/γ-Al_2O_3 Catalysts

	conversion of DBT (%)		
catalysts	280 °C	300 °C	320 °C
β-Mo_2C/γ-Al_2O_3-1[a]	56.7	81.3	96.1
β-Mo_2C/γ-Al_2O_3-2[b]	51.8	74.8	94.1
γ-Mo_2N/γ-Al_2O_3-1[c]	54.7	72.5	93.2
γ-Mo_2N/γ-Al_2O_3-2[d]	45.4	68.0	84.8

[a] Prepared by the HMT-based method. [b] Prepared by the TPRe method. (See the Supporting Information.) [c] Prepared by the HMT-based method. (See the Supporting Information.) [d] Prepared by TPRe method. (See the Supporting Information.)

It is well-known that the β-Mo_2C is an effective catalyst for the HDS. Herein, to testify the effectiveness of our new method, the catalytic activity of the as-prepared 23 wt % β-Mo_2C/γ-Al_2O_3 catalyst was evaluated using a DBT HDS reaction. As a comparison, the catalytic activities of a 23 wt % β-Mo_2C/γ-Al_2O_3 catalyst prepared by TPRe method and two 23 wt % γ-Mo_2N/γ-Al_2O_3 catalysts prepared by the HMT-based method and TPRe method were also tested. Their synthesis processes are given in the Supporting Information detailedly. The conversions of DBT on the four catalysts are summarized in Table 2. It can be seen that the as-prepared β-Mo_2C/γ-Al_2O_3 catalyst possesses good catalytic activity. The conversion of DBT on β-Mo_2C/γ-Al_2O_3 catalyst prepared by HMT-based method is slightly higher than by TPRe method. It proves that our new method is an effective route to synthesize active-supported molybdenum carbide catalyst. The slightly better performance of the catalysts formed from our new method than from TPRe method is probably because the two catalysts possess different surface areas and pore volumes. The BET surface area and pore volume of as-prepared 23 wt % β-Mo_2C/γ-Al_2O_3 (201.2 m^2 g^{-1} and 0.51 cm^3 g^{-1}, respectively) are higher than those prepared by TPRe method (146.3 m^2 g^{-1} and 0.40 cm^3 g^{-1}, respectively). The lower surface area and pore volume of the catalysts prepared by TPRe method than by this HMT-based method is possibly due to the longer time of heat treatment in TPRe method than the new method. The results are similar with our previous report, in which the BET surface of the Ni_2Mo_3N/MCM41 catalyst prepared by our new HMT-based method is larger than that prepared by TPRe method.[39] Furthermore, the HDS activity of as-prepared β-Mo_2C/γ-Al_2O_3 is higher than γ-Mo_2N/γ-Al_2O_3 catalyst with the same Mo loading prepared with HMT-based method, which is reasonable since it is well-known that molybdenum carbide possesses better HDS activity than molybdenum nitride.[15] At the same time, the HDS activities of both β-Mo_2C/γ-Al_2O_3 and γ-Mo_2N/γ-Al_2O_3 catalysts prepared by the HMT-based method are slightly higher than the β-Mo_2C/γ-Al_2O_3 and γ-Mo_2N/γ-Al_2O_3 prepared by TPRe method, respectively. It indicates that such a simple HMT-based method possesses potential to be a general and effective route to synthesize more active supported molybdenum nitride and carbide catalysts than the traditional TPRe method.

Conclusion

In summary, β-Mo_2C can be successfully prepared by a single-step heat treatment of a mixed salt precursor in argon atmosphere up to 700 °C, in which the mixture of molybdenum HMT complex with abundant HMT is used as precursor. The formation process shows that the β-Mo_2C is produced by the solid−solid carburization of γ-Mo_2N (derived from decomposition of molybdenum HMT complex) with the carbon-enriched pyrolysate (derived from decomposition of HMT). Furthermore, alumina-supported β-Mo_2C has also been successfully prepared by this simple method.

The nanocrystalline β-Mo_2C is well dispersed on the support. The evaluation of the catalytic activity of the as-prepared catalysts shows that the resultant catalyst exhibits good HDS activity. The results suggest that these syntheses provide a potential general route for the preparation of bulk β-Mo_2Cin large quantities and active supported molybdenum carbides catalysts.

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Supporting Information Available: The preparation of β-Mo_2C/γ-Al_2O_3 catalyst by the TPRe method and γ-Mo_2N/γ-Al_2O_3 catalysts by both the HMT method and the TPRe method. This material is available free of charge via the Internet at http://pubs.acs.org.

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