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Synthesis of bulk and alumina-supported γ-Mo_2N catalysts by a single-step complex decomposition method

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Abstract

A single-step complex decomposition method for the synthesis of bulk and alumina-supported γ-Mo_2N catalysts is described. The complex precursor $(HMT)_2(NH_4)_4Mo_7O_{24}\cdot 2H_2O$ (HMT: hexamethylenetetramine) is converted to γ-Mo_2N under a flow of Ar in a temperature range of 823–1023 K. Furthermore, decomposition of the precursor in a NH_3 flow forms γ-Mo_2N in a temperature range of 723–923 K. Compared with direct decomposition of the precursor in Ar, the reaction in NH_3 shows obvious advantages that the nitride forms at a lower temperature. In addition, alumina-supported γ-Mo_2N catalysts with different nitride loadings can be prepared from the alumina-supported complex precursor in the Ar or NH_3 flow. The resultant catalysts exhibit good dibenzothiophene HDS activities, which are similar to the γ-Mo_2N/γ-Al_2O_3 prepared by traditional TPR method. The catalyst prepared by decomposition in an Ar flow exhibits highest activity. It proves that such a single-step complex decomposition method possesses the potential to be a general route for the preparation of molybdenum nitride catalysts.

Keywords: γ-Mo_2N; γ-Mo_2N/γ-Al_2O_3; Synthesis; Complex decomposition; HDS

1. Introduction

In recent years, transition metal nitrides have gained growing interests because of their characters of rigidity, thermal stability quality, superconductivity, magnetism, and catalytic activity [1,2]. Molybdenum nitrides with high surface area possess good catalytic activity for certain reactions, similar to that of noble metal catalysts [3]. The material has been used as active catalysts for many reactions such as ammonia synthesis [4], ammonia decomposition [5], isomerization [6], NO hydrogenation [7], and hydrotreating [8–14]. In particular, the molybdenum nitride catalysts have been reported to have higher activities than frequently used sulfide catalysts and have demonstrated potential for use in both hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) process.

Since traditional synthesis of molybdenum nitrides requires severe conditions of temperature or pressure, research need to find novel synthesis approaches of molybdenum nitride have become intensive. One of the most commonly used routes to make large surface area molybdenum nitride is temperature-programmed reduction (TPR) method [9,15,16], in which MoO_3 precursor was treated in a flowing NH_3 at high space velocity (~6000 h^{-1}) at a slow rate (~1 K min^{-1}) to a high temperature (~973 K) [4–16]. The TPR method is proved to be an effective and general way to prepare active nitride catalysts. However, the rigorous synthesis conditions strongly affect the catalytic activity of the nitrides [17]. Development of new methods such as vapor deposition method [18,19], pyrolysis of metal complexes [20–23], and rapid solid-state metathesis (SSM) reactions [24] has gained increasing attention in recent years. In this regard, one of the simplest and most promising methods is single-step decomposition of a hexamethylenetetramine (HMT)-based complex. Afanasiev [23] has reported the synthesis of high surface area Mo_2N by means of thermal decomposition of $(HMT)_2(NH_4)_4Mo_7O_{24}$ at low temperature (823–1073 K). Bimetallic molybdenum nitrides and molybdenum carbide have also been prepared by this new method [25–27]. It suggests that this novel method could become a general route for the preparation of molybdenum nitrides.

Herein, we describe the synthesis of bulk and supported γ-Mo_2N catalysts by heat-treating bulk and supported $(HMT)_2(NH_4)_4Mo_7O_{24}\cdot 2H_2O$ complex precursor, respectively, in Ar or NH_3 flow. Decomposition of the complex at 823–1023 K in an Ar flow gets single-phase γ-Mo_2N. At the same time, thermal

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ammonolysis of $(HMT)_2(NH_4)_4Mo_7O_{24}\cdot 2H_2O$ precursor in a NH_3 flow can acquire single-phase γ-Mo_2N at a lower temperature. Amorphous γ-Mo_2N begins to form at a temperature as low as 723 K, and crystalline nitride is obtained at a higher temperature. Compared with that in an argon flow, the nitridation in a NH_3 flow can prepare nitride at a lower temperature. In order to get catalysts with high surface area or bifunctional catalysts, a series of alumina-supported γ-Mo_2N catalysts are also prepared by those methods. The resultant catalysts exhibit good HDS activity, which is similar with that of the γ-Mo_2N/γ-Al_2O_3 prepared by TPR method. The catalyst prepared by decomposition in an Ar flow exhibits the highest HDS activity.

2. Experimental

2.1. Synthesis of the catalysts

$(HMT)_2(NH_4)_4Mo_7O_{24}\cdot 2H_2O$ precursor was prepared by the following procedure: 1.41 g HMT was dissolved in 20 ml of deionized water and 6.20 g ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) was dissolved in 30 ml of deionized water. The HMT solution was dropwise added to the stirring $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ solution. After stirring for 0.5 h, white precipitates were formed. The solid was collected and rinsed with deionized water, followed by airing for 24 h and drying at 333 K for 3 h in air. The precursor was then heated in a quartz tube reactor under a flow of Ar or NH_3 at a mass rate of 1 h^{-1}. Temperature was increased linearly at a rate of 10 K min^{-1} and then kept at a given value for 2 h. The product was cooled under Ar or NH_3 and passivated for 6 h in a flow of 1% (v/v) O_2/N_2. Three samples were prepared at the temperature of 823 K, 923 K, and 1023 K in an Ar flow, as well as three samples were prepared at the temperature of 723 K, 823 K, and 923 K in a NH_3 flow, respectively.

Alumina-supported salt precursor was prepared by impregnation of γ-Al_2O_3 with an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and HMT at a fixed mole ratio of 1:2, which was obtained by dissolving the reagents in 15% $NH_3\cdot H_2O$ solution. The sample was then dried naturally for 48 h and dried at 313 K for 6 h. The precursor was heated at a rate of 10 K min^{-1} and kept at 823 K for 2 h under a NH_3 flow at a mass rate of 1 h^{-1}. While under an Ar flow at a mass rate of 1 h^{-1}, the final temperature was 923 K. The sample was cooled and passivated as described previously to obtain the supported nitride catalyst. γ-Mo_2N/γ-Al_2O_3 catalysts with different theoretical loadings were prepared. To evaluate catalytic activity, the precursor was pressed under 20.0 MPa and smashed to 20–40 mesh particles prior to heat treatment. For comparison, a 23 wt% γ-Mo_2N/γ-Al_2O_3 catalyst was also prepared by the TPR method. The synthesis was following the procedure described elsewhere [28].

2.2. Characterization of the catalysts

XRD characterization was conducted using a Rigaku D/max-2500 powder diffractometer employing Cu Kα radiation. Transmission electron microscope (TEM) images were acquired using a TECNAI G2 T20 high-resolution transmission electron microscope operating at 200 kV. The samples were dispersed in ethanol and treated with ultrasound for 5 min. Scanning electron microscopy (SEM) images were obtained using a LEO 1530VP scanning electron microscope. Single-point BET surface area and pore volume measurements employing nitrogen adsorption were acquired using a Micromeritics ASAP 2010 apparatus.

2.3. Catalytic activity

Catalytic activity of HDS of dibenzothiophene (DBT, 0.5 wt% in naphthane) was determined in the continuous mode in a fixed-bed micro-reactor that was heated by an oven. 1.2 g (~2.0 ml) catalyst was filled in the reactor and diluted with quartz powder to a volume of 5.0 ml. The catalyst was pretreated *in situ* with a flowing H_2 (30 ml/min) at 400 °C and at 0.3 MPa for 3 h. The evaluation was carried out under the following experimental conditions: reaction temperature of 280 °C, 300 °C, and 320 °C; feed rate of 10.0 ml h^{-1}; H_2 pressure of 3.0 MPa, and H_2 flow rate of 200 ml min^{-1}. In all cases, the liquid products were collected at a 1 h interval after a stabilization period of 5 h, and analyzed off-line by gas chromatography. For comparison purpose, the catalytic activity of a γ-Mo_2N/γ-Al_2O_3 catalyst prepared by TPR method was also evaluated.

3. Results and discussion

3.1. Preparation of the nitride catalyst in an Ar flow

Firstly, unsupported $(HMT)_2(NH_4)_4Mo_7O_{24}\cdot 2H_2O$ precursor was treated in an Ar flow at 823 K, 923 K, and 1023 K, respectively. The XRD results of the three products were shown in Fig. 1. The XRD pattern (Fig. 1A) of the sample prepared by treatment of the precursor at 823 K reveals very broad reflections that are characteristic of fcc Mo_2N structure, proving that amorphous γ-Mo_2N was formed. When the reaction temperature increases to 923 K, the intensity of γ-Mo_2N peaks detected in the sample pattern (Fig. 1B) enhances.

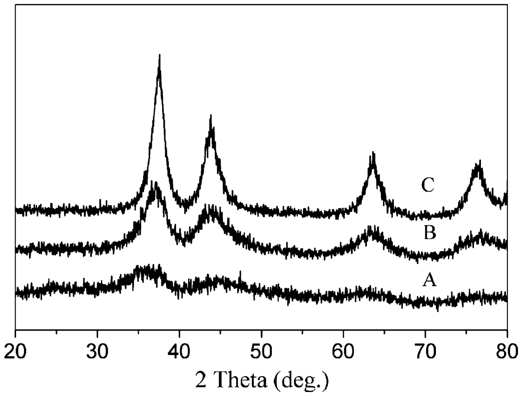

Fig. 1. XRD patterns of bulk complex precursor treated in an Ar flow at (A) 823 K, (B) 923 K, and (C) 1023 K.

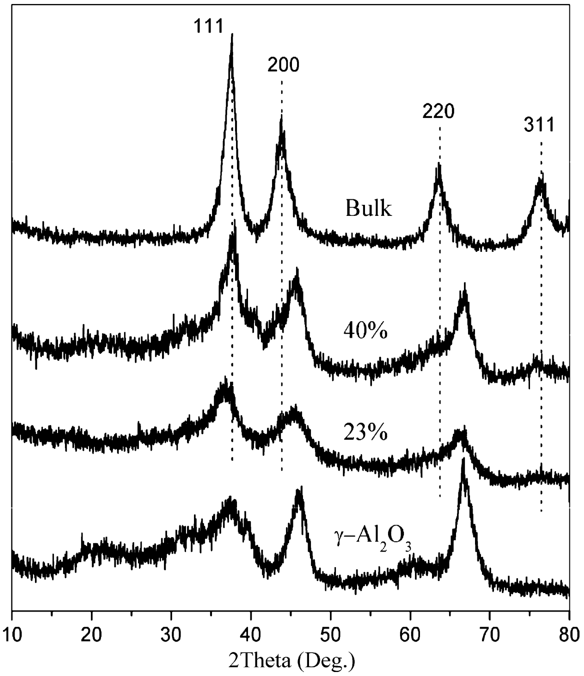

Fig. 2. XRD patterns of γ-Mo_2N/γ-Al_2O_3 catalysts with theoretical loadings of 23 wt% and 40 wt% prepared in an Ar flow. Also shown for comparison purpose are XRD patterns of γ-Al_2O_3 and bulk γ-Mo_2N.

After treating at 1023 K for 2 h, sharp reflections of γ-Mo_2N are observed in the XRD patterns (Fig. 1C). No impurities such as MoO_2, Mo or MoN are detected. It proves that the decomposition of the complex at 823–1023 K in an Ar flow can get single-phase γ-Mo_2N. The result is consistent with that reported by Afanasiev [23].

The successful synthesis of bulk γ-Mo_2N through this method led us to consider its applicability for the preparation of supported nitride as high surface area catalysts or bifunctional catalysts. A wet impregnation method was used to prepare γ-Al_2O_3-supported $(HMT)_2(NH_4)_4Mo_7O_{24}\cdot 2H_2O$ precursor. Then the precursor was treated in an Ar flow at 923 K. As showed in Fig. 2, a series of γ-Mo_2N/γ-Al_2O_3 catalysts with different nitride loadings were synthesized. No obvious XRD peaks of γ-Mo_2N are detected for loading of 23 wt%; owing to the small crystallite size of γ-Mo_2N on the support, which is below the detection limit of XRD. When the loading of the γ-Mo_2N increases to 40 wt%, the XRD patterns show some additional peaks located at ~43.5°, ~63.1° and ~75.7°, all associated to γ-Mo_2N. It indicates that the alumina-supported γ-Mo_2N can be prepared in a wide range of nitride loadings and crystallite sizes through this method. The BET surface area, pore volume, and average pore size of as-prepared 23 wt% γ-Mo_2N/γ-Al_2O_3 catalyst (Table 1) has been measured to be 245.4 $m^2\,g^{-1}$, 0.65 $cm^3\,g^{-1}$, and 10.5 nm, respectively. The BET surface area and pore volume of the catalyst prepared by decomposition in an Ar flow are obviously higher than those of the catalyst prepared by TPR method, while the average pore size is smaller (Table 1). This might because of the longer time of heat treatment in TPR method, which decreases the surface area, pore volume, and amounts of small pores of catalyst by agglomeration. The results are similar with our previous reports, in which the BET surface of the Ni_2Mo_3N/MCM41 catalyst prepared by this HMT-based complex decomposition method is larger than that prepared by TPR method [25]. TEM image of the as-prepared 23 wt% γ-Mo_2N/γ-Al_2O_3 catalyst is given in Fig. 3A. Observation of the image shows that fairly uniform γ-Mo_2N is not agglomerated but well dispersed on alumina, which is in good agreement with the XRD result. The morphology of the catalyst prepared by decomposition in an Ar flow is nearly the same as the catalyst prepared by TPR method (Fig. 3C).

3.2. Preparation of the nitride catalyst in a NH_3 flow

As reported by Sauls et al. [29], addition of NH_3 could increase the decomposition of organoaluminum amides to form AlN. Herein, we have tried to treat the precursor in a NH_3 flow. As shown in Fig. 4, the unsupported γ-Mo_2N is formed by treating $(HMT)_2(NH_4)_4Mo_7O_{24}\cdot 2H_2O$ precursor in a NH_3 flow. The XRD pattern (Fig. 4A) for the product obtained at 723 K shows broad peaks associated with fcc γ-Mo_2N, confirming the formation of nitride at such a low temperature. When the reaction temperature increases to 823 K, the intensity of the γ-Mo_2N peaks (Fig. 4B) enhances. After nitriding at 923 K for 2 h, the sharp reflections of γ-Mo_2N are observed (Fig. 4C). No impurities are detected. The results are similar as that of in an Ar flow, except that their reaction temperatures are different. The SEM image of the bulk γ-Mo_2N prepared at 823 K in a NH_3 flow is shown in Fig. 5. The morphology of the bulk γ-Mo_2N consists of homogeneously nucleated oval-shaped particles, which have an average particle size in the range of 1–2 μm and appear to be aggregated. It is notable that this morphology is quite different from the lamellar γ-Mo_2N prepared by Afanasiev [23]. It indicates that the intermediate

Table 1
The BET surface area, pore volume, average pore size, and HDS activity of as-prepared 23 wt% γ-Mo_2N/γ-Al_2O_3 catalysts

Catalysts	S_{BET} ($m^2\,g^{-1}$)	Pore volume ($m^3\,g^{-1}$)	Average pore size (nm)	Conversion of DBT (%)		
				553 K	573 K	593 K
γ-Mo_2N/γ-Al_2O_3-1[a]	189.5	0.59	12.4	45.4	68.0	84.8
γ-Mo_2N/γ-Al_2O_3-2[b]	245.4	0.65	10.5	54.7	72.5	93.2
γ-Mo_2N/γ-Al_2O_3-3[c]	208.4	0.63	12.0	46.3	65.4	84.0

[a] Prepared by TPR method.
[b] Prepared by decomposition in an Ar flow.
[c] Prepared by decomposition in a NH_3 flow.

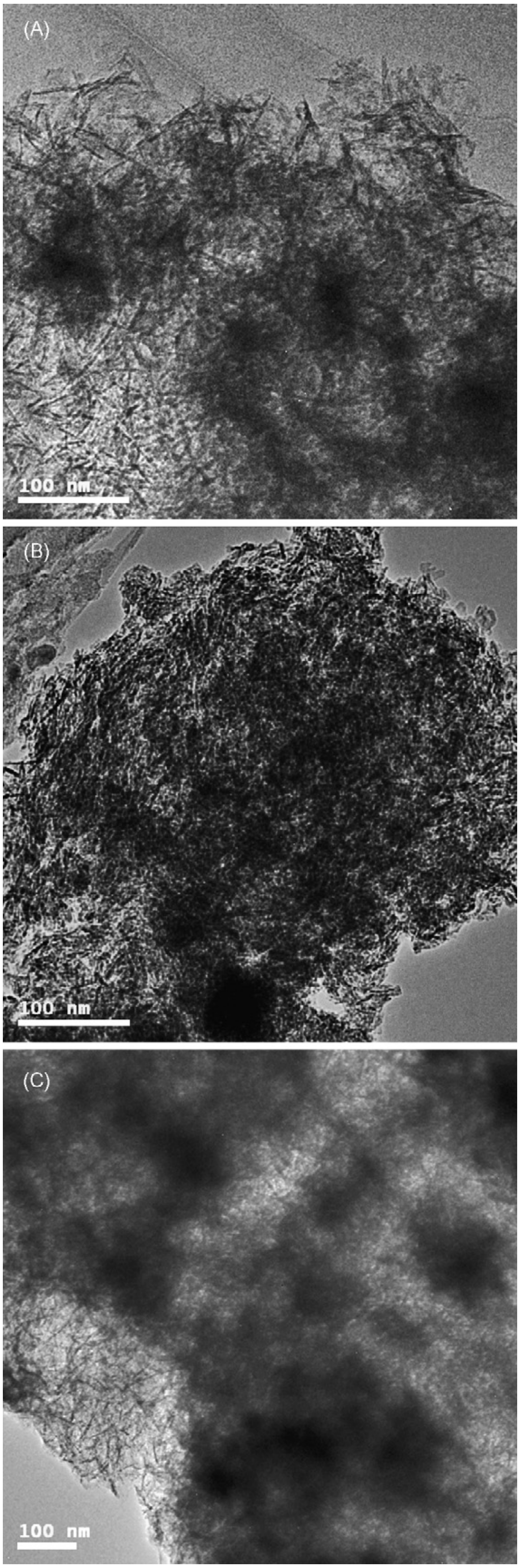

Fig. 3. TEM micrographs of the as-prepared 23 wt% γ-Mo_2N/γ-Al_2O_3 catalysts (A) by decomposition in an Ar flow, (B) by decomposition in a NH_3 flow, and (C) by TPR method (shown for comparison purpose).

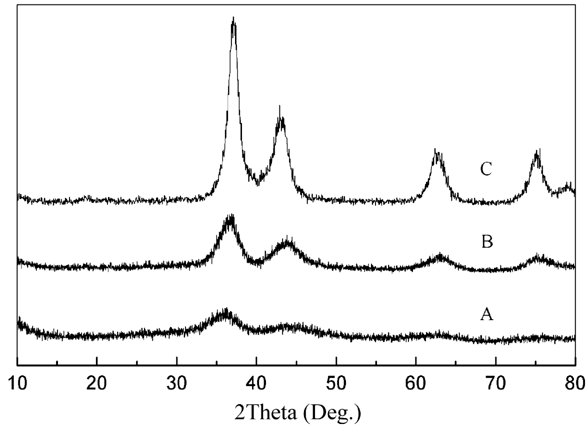

Fig. 4. XRD patterns of bulk complex precursor treated in a NH_3 flow at (A) 723 K, (B) 823 K, and (C) 923 K.

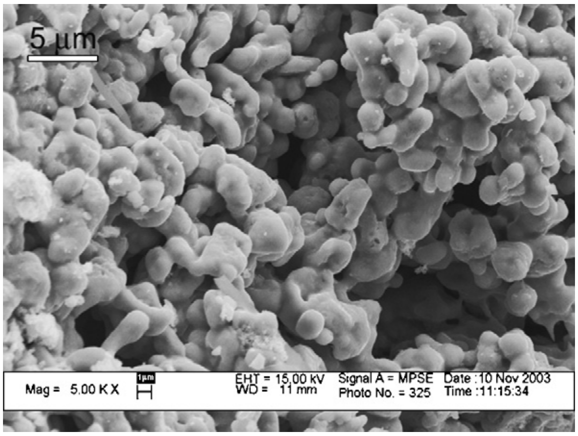

Fig. 5. SEM image of the γ-Mo_2N obtained at 723 K in a NH_3 flow.

during nitridation and decomposition of the precursor is different, which lead to the different forms of γ-Mo_2N following a topotactic route [23].

he above results indicate that phase-pure fcc γ-Mo_2N has been synthesized by decomposition of $(HMT)_2(NH_4)_4Mo_7O_{24}\cdot 2H_2O$ precursor in a NH_3 flow. Compared with the direct decomposition of the precursor in Ar atmosphere, the reaction in NH_3 atmosphere shows obvious advantage that γ-Mo_2N can be obtained at a lower temperature. The amorphous γ-Mo_2N begins to form at temperature as low as 723 K, which is about 100 K lower than that by direct decomposition in an Ar flow. The addition of ammonia could enhance the rate of decomposition of the precursor, which is in good agreement with the results reported by Sauls et al. [29].

As shown in Fig. 6, a series of γ-Mo_2N/γ-Al_2O_3 catalysts (15–40 wt% γ-Mo_2N) have been prepared by nitridation of alumina-supported $(HMT)_2(NH_4)_4Mo_7O_{24}\cdot 2H_2O$ precursors at 823 K for 2 h in a flowing NH_3. Just like the results in an Ar flow, no obvious XRD peaks associated with γ-Mo_2N are detected for the loadings below 23 wt%. When the loading of the γ-Mo_2N increases to 28 wt% and 40 wt%, the XRD patterns show some additional peaks of γ-Mo_2N. The alumina-supported γ-Mo_2N can be prepared in a wide range of γ-Mo_2N loadings and crystallite sizes with this route. The BET

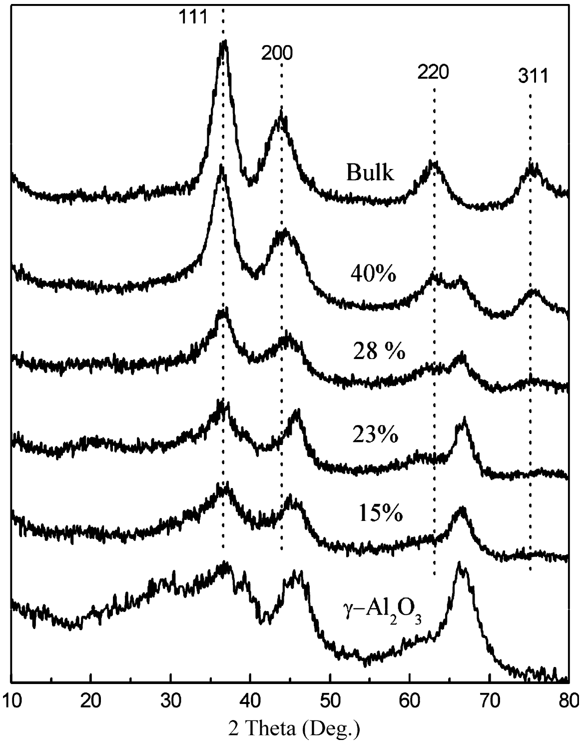

Fig. 6. XRD patterns of γ-Mo_2N/γ-Al_2O_3 catalysts with theoretical loadings of 15 wt%, 23 wt%, 28 wt%, and 40 wt% prepared in a NH_3 flow. Also shown for comparison purpose are XRD patterns of γ-Al_2O_3 and bulk γ-Mo_2N.

surface area, pore volume, and average pore size of as-prepared 23 wt% catalyst are 208.4 $m^2\ g^{-1}$, 0.63 $cm^3\ g^{-1}$, and 12.0 nm, respectively. The surface area and pore volume of the catalyst prepared by decomposition in a NH_3 flow are still lower than that of in an Ar flow, although the preparation temperature of the former is lower than that of the latter. This might because the decomposition in a NH_3 flow at low temperature brought on some residue of decomposition, which could block pores and cause the decrease of surface area. The TEM image of the 23 wt% γ-Mo_2N/γ-Al_2O_3 catalyst is shown in Fig. 3B. Its morphology is similar to that the catalyst prepared by decomposition in an Ar flow (Fig. 3A) and by TPR method (Fig. 3C), and the nitride is well dispersed on the support.

3.3. Catalytic activity

In order to testify the efficiency of this complex decomposition method, the catalytic property of both as-prepared 23 wt% γ-Mo_2N/γ-Al_2O_3 catalyst was measured for the HDS of DBT and compared with γ-Mo_2N/γ-Al_2O_3 catalyst with same metal loading prepared by traditional TPR method. As shown in Table 1, increasing the reaction temperature from 553 K to 593 K leads to an increase in the conversion of DBT for all the three catalysts. The catalyst prepared by decomposition in an Ar flow shows highest HDS activity. Its conversion of DBT is about 1.1–1.2 times higher than that on the catalysts prepared by TPR method and by decomposition in a NH_3 flow, while the latter two catalysts show nearly same activities.

The higher activity of the catalyst prepared by decomposition in an Ar flow than that by TPR method is in good agreement with our recent results [26], in which the HDS activity of supported molybdenum carbide catalyst prepared by the complex decomposition method is slightly higher than that by TPR method. It proves that this HMT-based complex decomposition method is an effective route to synthesize more active supported molybdenum nitride and carbide catalyst. Furthermore, the difference of catalytic activity of the three nitride catalysts should be due to the difference of their surface area and pore volume. The catalyst prepared by decomposition in an Ar flow possesses highest surface area and pore volume, thus it shows highest activity. However, although the catalyst prepared by decomposition in a NH_3 flow possesses slightly higher surface area and pore volume than that by TPR method, their HDS activities are similar. It might because the residue of decomposition in low temperature could cover some active sites and cause the decrease of activity.

4. Conclusion

$(HMT)_2(NH_4)_4Mo_7O_{24}\cdot 2H_2O$ can be used as precursor to prepare γ-Mo_2N under a flow of Ar in a temperature range of 823–1023 K. Decomposition of the complex precursor in a NH_3 flow also forms γ-Mo_2N in a temperature range of 723–923 K. Addition of ammonia can enhance the rate of decomposition of the precursor and reduce the reaction temperature. In addition, alumina-supported Mo_2N catalysts with different nitride loadings can be prepared from alumina-supported complex precursor in Ar or NH_3 flow. The resultant catalysts exhibit good dibenzothiophene HDS activity, which is very similar as that of the γ-Mo_2N/γ-Al_2O_3 prepared by TPR method. It proves that such a single-step complex decomposition method possesses potential as a general route for the preparation of molybdenum nitride catalyst.

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