

Dibenzothiophene hydrodesulfurization over alumina-supported β - $\text{Mo}_2\text{N}_{0.78}$ catalyst

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Abstract

γ -Alumina-supported β - $\text{Mo}_2\text{N}_{0.78}$ catalyst was synthesized by the temperature-programmed nitriding reaction and tested to determine its catalytic activity and selectivity during the hydrodesulfurization (HDS) of dibenzothiophene. The results indicated that the conversion increases with reaction temperature and hydrogen pressure. And increasing the hydrogen pressure results in more hydrogenation, but increasing reaction temperature can improve the two parallel pathways of direct desulfurization and hydrogenation desulfurization at same degree. Sulfur can replace the surface oxygen of passivated nitride in the HDS reaction although the bulk structure is preserved.

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1. Introduction

An increasing interest has developed in exploring the catalytic properties of molybdenum nitrides because they resemble group VIII metals in a number of hydrogen involved reactions, which include CO hydrogenation [1], NH_3 synthesis [2] and hydrotreating (HDN, HDS) [3–5] reactions, etc. Studies have shown that the alumina-supported γ - Mo_2N is more active than molybdenum sulfided catalysts for the HDSs of thiophene, benzothiophene and dibenzothiophene [5–8]. Nagai et al. [5] found that γ - Mo_2N has extremely selective activity for the C–S bond breakage of dibenzothiophene to form biphenyl. Both Abe and Bell [8], and Markel and Van Zee [9] found unsupported γ - Mo_2N is active for HDS of benzothiophene or thiophene, and the study also showed that the bulk structure of the γ - Mo_2N is preserved despite the sulfiding conditions present in the catalytic reactor. Recently some research found that γ - Mo_2N will be transformed to β - $\text{Mo}_2\text{N}_{0.78}$ when it is heated in He [10], and Nagai et al.

[11] once synthesized pure β - $\text{Mo}_2\text{N}_{0.78}$ when they replaced NH_3 with He to cool down the product of temperature-programmed reaction of MoO_3 and NH_3 . We synthesized the pure β - $\text{Mo}_2\text{N}_{0.78}$ via the temperature-programmed reaction of MoO_3 and N_2 - H_2 mixture gases, and found that it is more active than molybdenum sulfide in thiophene's HDS reaction [12]. In this paper, the γ -alumina-supported β - $\text{Mo}_2\text{N}_{0.78}$ catalyst was prepared with N_2 - H_2 mixture gases, and its HDS activity and selectivity of dibenzothiophene is first reported.

2. Experiment

Alumina-supported molybdenum oxide precursors with various Mo loadings were prepared by impregnation of γ - Al_2O_3 with aqueous solutions of ammonium heptamolybdate. Catalysts with loading above 10 wt.% required multiple impregnations. Following impregnation, catalysts were dried 3 h at 393 K and then calcined 5 h in air at 773 K.

Alumina-supported nitrides were produced according to the reference [12]. The precursor of catalyst was packed on the center of a quartz tube reactor, and was treated with

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N_2-H_2 from room temperature to 573 K at a heating rate of 10 K min^{-1} , from 573 to 773 K at 0.6 K min^{-1} , then from 773 to 973 K at 2 K min^{-1} and hold at this temperature for 2 h. After the nitriding reaction, the reactor was cooled down to room temperature under N_2 , and then passivated with a mixture of 1% O_2 in N_2 for 2 h.

Bulk crystal structures of catalyst were determined using X-ray diffraction (XRD). Specific surface area of catalyst was evaluated by applying the BET method to the nitrogen adsorption isotherms measured at 77 K. The Mo K-edge EXAFS spectra were collected at the beamline of 1W1B, the XAFS station of the Beijing Synchrotron Radiation Facility (BSRF). The electron storage ring was operated at 2.2 GeV with a typical current of 80 mA.

Temperature-programmed reduction (TPR) experiments were carried out in 10% H_2 in Ar (by volume) with a flow rate of 30 ml/min and a temperature ramping rate of 10 K/min. TPR profiles were recorded with a thermal conductivity detector. The TPR experiment of molybdenum sulfide was performed in situ after sulfuration of molybdenum trioxide. The sulfuration was carried out using a 3% CS_2 /cyclohexane mixture at 623 K for 2 h and the H_2 flow rate of 20 ml/min.

The activity measurement for dibenzothiophene HDS was carried out in the high pressure autoclave for 1 h. The reaction material is 0.5 wt.% dibenzothiophene in cyclohexane and the liquid products of HDS was analyzed by gas chromatogram.

3. Results and discussion

XRD patterns of molybdenum precursor before and after nitridation are shown in Fig. 1. The appearance of MoO_3 diffraction peaks besides that of $\gamma-Al_2O_3$ indicates that the precursor is $MoO_3/\gamma-Al_2O_3$. After nitridation with N_2-H_2 mixture gases, the diffraction peaks of MoO_3 disappear and a number of $\beta-Mo_2N_{0.78}$ diffraction peaks are observed. These

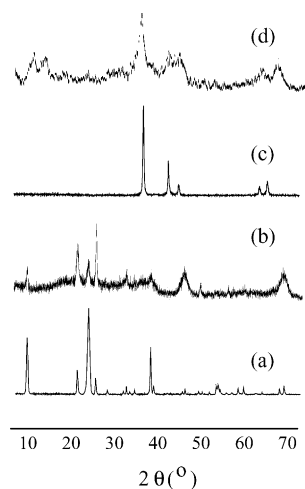


Fig. 1. XRD patterns of: (a) MoO_3 ; (b) molybdenum precursor (30 wt.%); (c) $\beta-Mo_2N_{0.78}$; (d) $\beta-Mo_2N_{0.78}/\gamma-Al_2O_3$ (30 wt.%).

Table 1

The BET surface area of catalyst with different Mo loading

Mo loading (wt.%)	Crystal phase ^a	S_{BET} ($m^2\text{ g}^{-1}$)
0	$\gamma-Al_2O_3$	160
5	$\gamma-Al_2O_3$	144
10	$\gamma-Al_2O_3$	142
20	$\beta-Mo_2N_{0.78}/\gamma-Al_2O_3$	128
30	$\beta-Mo_2N_{0.78}/\gamma-Al_2O_3$	125

^a Catalyst phase determined by XRD patterns.

results indicate that MoO_3 is transformed to $\beta-Mo_2N_{0.78}$ by nitridation and $\beta-Mo_2N_{0.78}/\gamma-Al_2O_3$ is synthesized via temperature-programmed reaction.

For samples with Mo loading below ~ 10 wt.%, only diffraction of $\gamma-Al_2O_3$ supporter is observed in XRD patterns. At high loadings (≥ 20 wt.%), a number of diffraction peaks of $\beta-Mo_2N_{0.78}$ phase are observed. It indicates that molybdenum nitride formed and highly dispersed on the surface of alumina supporter when the loading amount of Mo is low. The specific surface area of catalyst with different Mo loading is shown in Table 1. The surface area slowly decreases with increase of Mo loading when it is low (≤ 10 wt.%) or high (≥ 20 wt.%), but decreases greatly when Mo loading increases from 10 to 20 wt.%, which indicates that alumina support is fully covered by Mo species in the Mo loading of 10–20 wt.%. Thus, we attempted to apply XANES spectroscopy to elucidate structural details. Mo K-edge XANES spectra and Fourier transform of the EXAFS oscillations for several compounds and catalysts are shown in Fig. 2. Before nitriding reaction, the spectral of $MoO_3/\gamma-Al_2O_3$ is almost similar to ammonium heptamolybdate, which is distorted octahedral. It suggests that dominant Mo species on alumina support are also in poor order. After nitriding, structural change can be clearly seen in XANES, and the spectral of supported nitride is similar to unsupported nitride. There is only one large peak at about 0.136 nm for standard compound $Na_2MoO_4 \cdot 2H_2O$ on its radial structure functions (RSFs), which represents the four nearest oxygen neighbors. The Mo–O distances are 0.176 nm according to the literature [13], so the position of the peak of RSF is downshifted from the true distance by about 0.04 nm. Three major peaks on the RSF of $MoO_3/\gamma-Al_2O_3$ crystalline are observed, the first two represent six nearest neighbor oxygen atoms around the Mo atom and the third large peak is due to the next nearest neighbors, which are consistent with previous reports [14]. There are three major peaks on the RSF of unsupported $\beta-Mo_2N_{0.78}$ at about 0.161, 0.258 and 0.380 nm, respectively. For alumina-supported oxide after nitridation, three peaks are located almost at the same positions as those of $\beta-Mo_2N_{0.78}$ crystalline, which indicates that Mo oxide transforms to $\beta-Mo_2N_{0.78}$ through nitriding reaction. And the magnitude of the third peak greatly decreases on the RSF of supported nitride compared with that of unsupported. This result suggests that the Mo species are well dispersed on the surface of support.

The main products for HDS of dibenzothiophene on $\beta-Mo_2N_{0.78}/\gamma-Al_2O_3$ catalyst are biphenyl (BP) and cyclo-

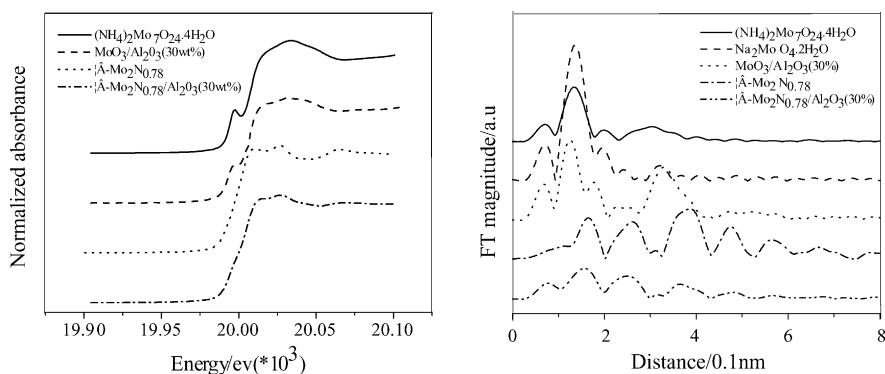


Fig. 2. Mo K-edge XANES spectra (left) and radial structure function (right) of $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ and $\beta\text{-Mo}_2\text{N}_{0.78}/\gamma\text{-Al}_2\text{O}_3$ catalysts.

hexylbenzene (CHB), and minority hexahydrodibenzothio-
 iophene and tetrahydrodibenzothio-
 iophene are also created. So the HDS reaction goes through two parallel pathways:
 (i) direct desulfurization to yield BP, and (ii) hydrogenation followed by desulfurization to yield CHB, which like
 previous results about HDS of dibenzothio-
 iophene on $\gamma\text{-Mo}_2\text{N}$ [5]. In addition, our experiment result showed that 26% BP
 can be converted to CHB when 0.5 wt.% BP in cyclohexane
 at 593 K and 12 MPa hydrogen pressure with 10% Mo
 loading catalyst, which indicates that BP can further convert
 to CHB by hydrogenation. Nagai et al. [5] once reported that
 BP is not hydrogenated to form CHB on alumina-supported
 $\gamma\text{-Mo}_2\text{N}$ catalyst, which indicates that $\beta\text{-Mo}_2\text{N}_{0.78}$
 has stronger hydrogenation capacity than $\gamma\text{-Mo}_2\text{N}$.

The results of DBT HDS at different temperature are
 shown in Table 2. It shows that the DBT conversion increases
 with increasing of temperature, and the BP selectivity almost
 unchanged at these temperatures, which indicates that the re-
 action temperature increasing can improve the two parallel
 pathways at same degree.

The effect of hydrogen pressure on the conversion of
 DBT at 593 K is shown in Table 3. The conversion of DBT
 increases with increasing of hydrogen pressure, and the
 selectivity of BP decreases with the pressure increasing. It
 indicates that high hydrogen pressure is favorable for the
 hydrogenation of DBT. The decrease of BP selectivity is
 also because that some BP can be further hydrogenated to
 form CHB at high hydrogen pressure.

Table 2

The influence of different reaction temperatures on conversion and selectivity of catalyst

Catalyst (wt.% Mo)	Reaction factors		Results	
	Temperature (K)	Pressure (MPa)	Conversion (%)	HDS selectivity ^a
10	523	6.8	13	4.88
10	563	7	56	4.56
10	593	7	93	4.88
No	623	14	2	–

^a The HDS selectivity represents the molar ratio of biphenyl/
 cyclohexylbenzene.

We reported that the bulk structure of $\beta\text{-Mo}_2\text{N}_{0.78}$ cata-
 lyst was kept after thiophene HDS reaction at 633 K for 9 h
 in our previous work [12]. The Mo K-edge XANES spectra
 and RSF of supported nitride after HDS of dibenzothio-
 iophene at 563 K is shown in Fig. 3. It can be seen that after HDS re-
 action, XANES spectra and RSF have slightly change, which
 indicates that the structure of catalyst is preserved after HDS
 reaction.

Several groups [15–16] reported the result of surface sul-
 furation of $\gamma\text{-Mo}_2\text{N}$ catalysts. In this study, $\text{H}_2\text{-TPR}$ exper-
 iment is also used to deeply indicate the change of catalyst
 properties after HDS. The TPR profiles of unsupported and
 supported passivated catalyst are shown in Fig. 4. Compared
 with free passivated $\beta\text{-Mo}_2\text{N}_{0.78}$, passivated $\beta\text{-Mo}_2\text{N}_{0.78}$
 shows two hydrogen consumption peaks, which indicates that
 the peak at about 700 K is caused by reduction of surface ox-
 ide species created during passivate reaction. The same phe-
 nomenon was also observed in TPR character of $\gamma\text{-Mo}_2\text{N}$
 [17]. The TPR profile of $\beta\text{-Mo}_2\text{N}_{0.78}/\gamma\text{-Al}_2\text{O}_3$ shows two
 hydrogen consumption peaks and they are similar to those of
 unsupported $\beta\text{-Mo}_2\text{N}_{0.78}$ basis on the temperature position.
 After HDS reaction, it can be seen that the 700 K reduction
 peak of supported $\beta\text{-Mo}_2\text{N}_{0.78}$ catalyst becomes very weak
 and a new reduction peak at about 540 K is observed corre-
 spondingly. Compared with the TPR profile of molybdenum
 sulfide, the new peak formation can be attributed to the sulfa-
 ration of molybdenum nitride in the condition of HDS. There
 is a high temperature reduction peak above 1000 K for molyb-
 denum sulfide, but it is not observed for the nitride catalyst

Table 3

The influence of different reaction pressure on conversion and selectivity of catalyst

Catalyst (wt.% Mo)	Reaction factors		Results	
	Temperature (K)	Pressure (MPa)	Conversion (%)	HDS selectivity ^a
10	593	7	93	4.88
10	593	10	98	1.33
10	593	14	100	0.54

^a The HDS selectivity represents the molar ratio of biphenyl/
 cyclohexylbenzene.

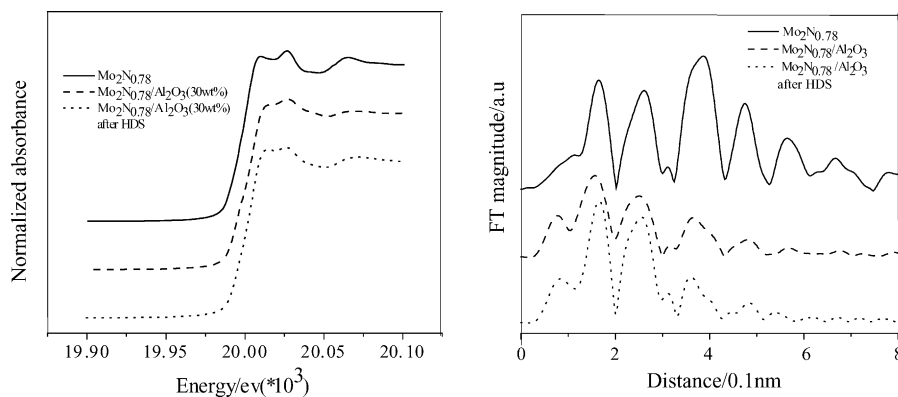


Fig. 3. Mo K-edge XANES spectra (left) and radial structure function (right) of β - $\text{Mo}_2\text{N}_{0.78}/\gamma$ - Al_2O_3 catalysts after HDS reaction.

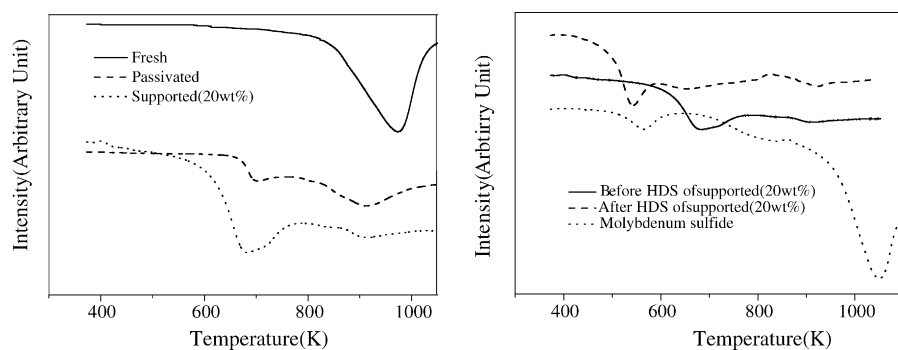


Fig. 4. The TPR profiles of β - $\text{Mo}_2\text{N}_{0.78}/\gamma$ - Al_2O_3 catalyst before and after HDS reaction.

after HDS. These results indicate that β - $\text{Mo}_2\text{N}_{0.78}/\gamma$ - Al_2O_3 catalyst surface is slightly sulfided, which results from sulfur replaces the surface oxygen of passivated nitride in the HDS condition although the bulk structure is preserved.

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