Hydrodesulfurization of 4,6-DMDBT on a multi-metallic sulfide catalyst with layered structure

Lu Wang, Yongna Zhang, Yuliang Zhang, Peng Liu, Hongxian Han, Min Yang, Zongxuan Jiang*, Can Li*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, China

ABSTRACT

A multi-metallic NiAlMoW catalyst with layered structure was prepared by surfactant-assisted co-precipitation method using NiAl-layered double hydroxide (NiAl-LDH) as the structure-directing template. By carefully tuning the composition of the layered structure and the synthesis conditions, we have prepared a series of Ni_mAl_nMoW catalysts. For the HDS of 4,6-DMDBT, $NiAl_3MoW$-5 shows two times higher intrinsic catalytic activity (based on weight of active metals) compared to that of the commercial $CoNiMoW/Al_2O_3$ catalyst. The sulfur content in the model compound could be reduced from 500 ppm to less than 20 ppm using this catalyst under the operation conditions of 3.0 MPa, 300 °C, a WHSV (weight hourly space velocity) of 9 h^{-1}, and H$_2$/oil ratio of 800 Nm^3/m^3. The synthesized catalysts were characterized by SEM, TEM, XRD, TG/DSC, nitrogen adsorption/desorption isotherms and XRF. This NiAlMoW catalyst has retained the unique layered structure of NiAl-LDH, which can facilitate uniform dispersion of the active species on both the surface and the edge of the layer. It was found that the layered structure has a great impact on the catalytic activity of the HDS reactions.

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1. Introduction

Ultra-deep hydrodesulfurization (HDS) of fuel oils has received much attention nowadays due to increasingly stringent environmental regulations enacted throughout the world [1–4]. Though traditional HDS catalysts are highly efficient in removing thiols, sulfides, and disulfides, they are inefficient in ultra-deep desulfurization of refractory sulfur-containing compounds, such as 4,6-dimethydibenzothiophene (4,6-DMDBT). Therefore, development of novel HDS catalysts with super high activity is needed [5–14].

In order to achieve ultra-deep desulfurization, many researches have been conducted including development of novel phosphide, carbide, and nitride catalysts, and improvement of existing sulfide catalysts by doping with noble metals and loading into zeolites [15–18]. In recent years, an unsupported NiMoW tri-metallic HDS catalyst, called NEBULA, has been drawing much attention, [19–21] because its HDS activity is much higher than those of other conventional catalysts. Different methods have been applied for the synthesis of such NiMoW catalyst. Soled et al. have synthesized

NiMoW sulfide catalysts by sulfidation of an amorphous Ni–Mo–W oxide precursor prepared by the methods of boiling decomposition, direct precipitation or pH-controlled precipitation [19]. Nava et al. have prepared unsupported Ni–Mo–W sulfide catalysts by in situ activation of tri-metallic Ni–Mo–W alkyl precursors during the HDS of dibenzothiophene (DBT) [22].

In our previous work, we also reported that a tri-metallic NiMoW catalyst obtained by surfactant-assisted co-precipitation method [23] exhibits high intrinsic HDS activity, as well as providing excellent catalytic performance in the HDS of actual diesel. The high HDS catalytic performance was partially attributed to the unique hydrotalcite-like multi-layered structure in the NiMoW sulfide catalyst according to the structural characterization. However, this catalyst is not cost effective because it is composed of bulk NiMoW sulfide without using any support.

In this work, a novel multi-metallic NiAlMoW catalyst with layered structure has been synthesized using NiAl-LDH material as structure-directing template. Layered double hydroxides (LDHs) are one of the most useful layered inorganic compounds; they thus receive considerable attention in the field of catalysis [24–27]. LDHs are a class of materials with a general formula of $[M^{II}_{1-x}M^{III}_x(OH)_2][A^{n-}_{x/n} \cdot mH_2O]$, where M^{II} and M^{III} represent di- and trivalent metal ions within the brucite-like layers, respectively, and A^{n-} means interlayer anions. They are usually comprised of positively charged layers of mixed metal hydrox-

Table 1
The physicochemical properties and catalytic activity of the Ni$_3$AlMoW-p catalysts.

Catalysts	pH value[a]	Surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)	Sulfur content in product (ppm)	Specific HDS activity[b]
Ni$_3$AlMoW-3	3	104	5.8	0.1503	34	339
Ni$_3$AlMoW-5	5	96	7.5	0.1814	18	568
Ni$_3$AlMoW-7	7	107	8.0	0.2151	27	406
Ni$_3$AlMoW-9	9	147	4.8	0.1758	40	302
Commercial CoNiMoW/Al$_2$O$_3$	–	125	8.5	0.2641	127	100

[a] The pH values are adjusted by HNO$_3$ and NH$_3$·H$_2$O in the ion exchange process.
[b] The HDS activity of the commercial reference catalyst is defined as 100. The feedstock is 4,6-DMDBT as a model sulfur containing molecule in decalin (sulfur content of 500 ppm). The HDS reaction is operated at the mild condition of 573 K, 3.0 MPa, WHSV of 9 h^{-1}, and a H$_2$/oil ratio of 800 Nm^3/m^3.

Table 2
The composition and HDS activity of Ni$_m$Al$_n$MoW-5 catalysts.

Catalysts	Specific HDS activity	Intrinsic HDS activity[a]	Active metal content[b]	Compound formula[c]
NiMoW[d]	700	214	77.3%	9.4NiO MoO$_3$·2.3WO$_3$
Ni$_3$AlMoW	568	189	71.4%	0.4Al$_2$O$_3$ 3.9NiO 1.1MoO$_3$ WO$_3$
NiAlMoW	312	117	63.5%	1.2Al$_2$O$_3$ 3.4NiO 1.2MoO$_3$ WO$_3$
NiAl$_3$MoW	401	198	48.1%	3.8Al$_2$O$_3$ 3.7NiO 1.2MoO$_3$ WO$_3$
NiAl$_5$MoW	234	140	39.7%	6Al$_2$O$_3$ 3.7NiO 1.2MoO$_3$ WO$_3$
Commercial CoNiMoW/Al$_2$O$_3$	100	100	23.7%	13Al$_2$O$_3$ 0.5Co$_3$O$_4$ 1.1NiO 3MoO$_3$ WO$_3$

[a] The intrinsic HDS activity means the HDS activity of per unit weight of active metal.
[b] The active metal includes Co, Ni, Mo and W.
[c] Compound formula is determined by the XRF results of catalyst.
[d] The unsupported NiMoW catalyst is reported in our previous work [23].

ides and exchangeable anions located in the interlayer gallery for charge balance [28–30]. The synthesized multi-metallic catalyst was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD). It was found that the active metals species are highly dispersed on the multi-layered structure, which might be responsible for the high intrinsic HDS activity. The optimized NiAl$_3$MoW-5 catalyst shows about two times higher HDS activity than that of the commercial CoNiMoW/Al$_2$O$_3$ catalysts. Thus, the cheap metal Al has been introduced into the catalyst by adjusting the composition of NiAl-LDH layers while maintaining the high HDS catalytic activity.

2. Experimental

2.1. Synthesis of catalysts

The sulfide catalyst was synthesized in two steps. Firstly, the slurry of NiAl-LDH precursor was prepared by surfactant-assisted co-precipitation method from the starting materials of Ni(NO$_3$)$_2$·4H$_2$O and Al(NO$_3$)$_3$·6H$_2$O according to the procedure reported in the literature [31,32]. Typically, a solution of NaOH was added dropwise into the nitrate solution containing one of several different Ni/Al molar ratios (denoted as m/n hereafter) at 85 °C. During the initial co-precipitation stage, the slurry was stirred vigorously and the pH value was adjusted to 8 using NaOH solution. The reaction mixture was kept stirring at 85 °C continually for 24 h under N$_2$ atmosphere. The precipitate was washed with an adequate amount of deionized water to remove Na$^+$ and then dried at 120 °C overnight. The obtained material is denoted as Ni$_m$Al$_n$-NO$_3$; it forms the NiAl-LDH slurry upon dissolving in a mixed solvent of deionized water and ethylene glycol. The precursors of NiAlMoW catalysts (denoted as Ni$_m$Al$_n$MoW-p, where m and n correspond to the initial Ni/Al molar ratio in the preparation of NiAl-LDH and p corresponds to the pH value in the ion exchange reaction) were obtained by ion exchange of NiAl-LDH slurry with (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (molybdenum source) and (NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$·xH$_2$O (tungsten sources) at different pH values of p in the mixed solvents containing ethylene glycol, water and Triton X-100. The molar ratio of Ni/Mo/W in the precursors of NiAlMoW catalysts was 3.6/1/1. The reactions were carried out at 85 °C

for 6 h under the N$_2$ flow. Then the Ni$_m$Al$_n$MoW-p precursors were sulfided at 400 °C for 2 h in the flow of 10 vol% H$_2$S/H$_2$ mixed gas with the flow rate of 60 ml/min to obtain the final sulfide NiAlMoW catalyst.

The effects of the experimental conditions and the Ni/Al molar ratios on the HDS activities of the NiAlMoW catalysts are listed in Tables 1 and 2, respectively. In a typical preparation of Ni$_3$AlMoW-5 catalyst, Ni$_3$Al-LDH material was firstly obtained from the reaction between Ni(NO$_3$)$_2$·4H$_2$O (0.036 mol) and Al(NO$_3$)$_3$·6H$_2$O (0.012 mol). Then the precursor of catalyst was prepared by an ion-exchange reaction between the slurry of Ni$_3$Al-LDH (0.036 mol Ni^{2+}) and (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (0.01 mol Mo^{6+}) and (NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$·xH$_2$O (0.01 mol W^{6+}) at pH values of 5 in the mixed solvents.

2.2. Catalytic reaction

The HDS reaction with the model compound of 4,6-DMDBT in decalin (sulfur content 500 ppm) was operated at a flowing fixed-bed micro-reactor under the conditions of 3.0 MPa, 300 °C, a WHSV (weight hourly space velocity) of 9 h^{-1}, and H$_2$/oil ratio of 800 Nm^3/m^3. It should be noted that the catalyst was sulfided at 400 °C for 2 h in the flow of 10 vol% H$_2$S/H$_2$ prior to HDS reaction. The outflow samples were cooled down and collected hourly; each was washed with 2 M NaOH solution. The total sulfur content in the samples was determined by Antek 9000S total sulfur analyzer (detection limitation, 0.1 ng/μl). In a typical HDS reaction, 0.5 g catalyst was added into the reactor and presulfided at 400 °C for 2 h. Then the reaction temperature was cooled down to 300 °C. The feedstock was pumped into the reactor with the flow rate of 0.075 ml/min. The HDS reaction was operated for 10 h in order to evaluate the deactivation of the catalyst. However, all the catalysts exhibited stable performance and could achieve the equilibrium after 5 h. So the product sample was collected after 7 h and the total sulfur content was tested. The commercial catalyst CoNiMoW/Al$_2$O$_3$ obtained from SINOPEC was used as the reference catalyst. This commercial catalyst is one of the best HDS catalysts used in China and exhibits good HDS performances in industrial applications.

The specific HDS activity was calculated by the following equation [23]:

$$R = 100 \frac{(1/S_p)^{0.65} - (1/S_f)^{0.65}}{(1/S_{pr})^{0.65} - (1/S_{fr})^{0.65}}$$

Here, S_p and S_f stand for the sulfur content in the product and feedstock using NiAlMoW catalysts, respectively, while S_{pr} and S_{fr} stand for the sulfur content in the product and feedstock using the commercial catalyst, respectively. The equation of the specific HDS activity is an experimental formula, where the exponent of 0.65 means that the order of HDS reaction is 1.65. The order of reaction is determined by the overall consideration of reaction conditions in hydrodesulfurization of actual diesel.

2.3. Characterization

XRD patterns were recorded on a Rotaflex (Ru-200b) powder X-ray diffractometer with CuKα radiation. Diffraction patterns were collected at a speed of 5° min^{-1}. Elemental analyses of the Al and active metals contents were conducted on a Magix-2424 X-ray fluorescence (XRF) spectrometer. The surface area was measured by N$_2$ adsorption/desorption technique performed at liquid nitrogen temperature on a Micrometrics ASAP-2000 system with a static measurement mode. All the samples were degassed at 120 °C for 6 h prior to each measurement. All TG/DSC experiments were carried out in a SETSYS 16/18 high-performance modular simultaneous TG/DSC thermal analyzer, which was purged under nitrogen flow for 30 min prior to the measurement. The runs were performed under nitrogen flow with a continuous flow rate of 80 mL/min, and with the increment of the temperature at a rate of 10 °C/min starting from room temperature to 800 °C. The morphology and the dispersion of the catalysts were studied by SEM and HRTEM. SEM images were examined with a Quanta 200F instrument. HRTEM images were obtained on a Tecnai G2 F30 S-Twin (FEI Company) instrument.

3. Results and discussion

In this work, alcohol and surfactant were used to improve the dispersion of the active species and to control the morphology of the catalyst [12,11]. Furthermore, in the preparation of NiAl-MoW precursors, molybdate and metatungstate anions could be exchanged with NO$_3$$^-$ anion bonded to positive sheets in the interlayer galleries of the NiAl-LDH. And since the reaction occurred at liquid–solid interfaces between the soluble molybdenum and tungsten salts and the slurry of the NiAl-LDH, it is expected that the layered structure of the NiAl-LDH could be well maintained in the final NiAlMoW catalyst, which is in good agreement with the following XRD results.

The powder XRD patterns of Ni$_3$Al-LDH (Ni/Al = 3) and the Ni$_3$AlMoW-p precursors are shown in Fig. 1. It should be noted that the characteristic peaks due to the diffraction of the (0 0 3) plane of LDH were shifted from ~10.5° in Ni$_3$Al-LDH to ~7.2° in Ni$_3$AlMoW-p precursors, suggesting that the value of d(0 0 3) spacing increased from ~0.84 nm to ~1.23 nm after the ion exchange reaction. The value of d(0 0 3) spacing could approximately represent the separation of the two neighbouring LDH layers, which includes the thickness of the LDH host and the gallery height of the interlayer region. So, the expansion of the d(0 0 3) spacing is an indication that the molybdate and metatungstate anions are successfully exchanged into the galleries of the LDH layers.

Additionally, one should note that the XRD peaks due to diffraction of the (1 1 0) plane of LDH are detected at ~61° with d-spacing of ~0.153–0.149 nm for all samples; the presence is not affected by
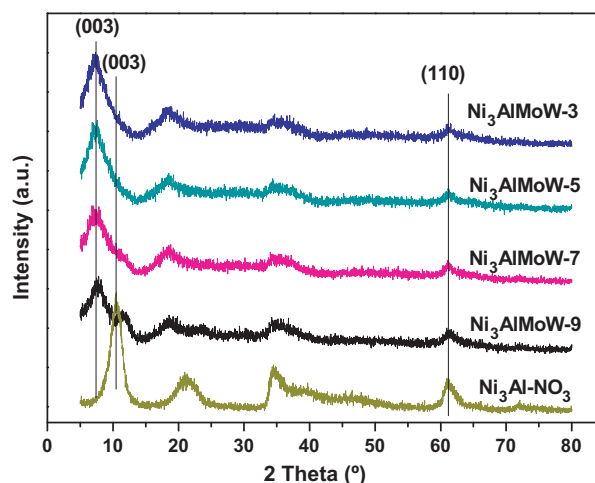
Fig. 1. XRD patterns of Ni$_3$Al-LDH (Ni/Al = 3) and the Ni$_3$AlMoW-p precursors prepared under different pH values. The expansion of the d(0 0 3) spacing of NiAl-LDH indicates the exchange of Mo and W species into the galleries of the LDH layers. The d(0 0 1) spacing indicates the reservation of layer-structure in the NiAlMoW precursors.

the size of the interlayer anions [27]. This indicates that the layered structure of LDH is well preserved in the NiAlMoW precursors.

TG/DSC curves for the Ni$_3$Al-LDH and Ni$_3$AlMoW-5 catalysts are shown in Fig. 2. In the curves of Ni$_3$Al-LDH (Fig. 2(a)), there are

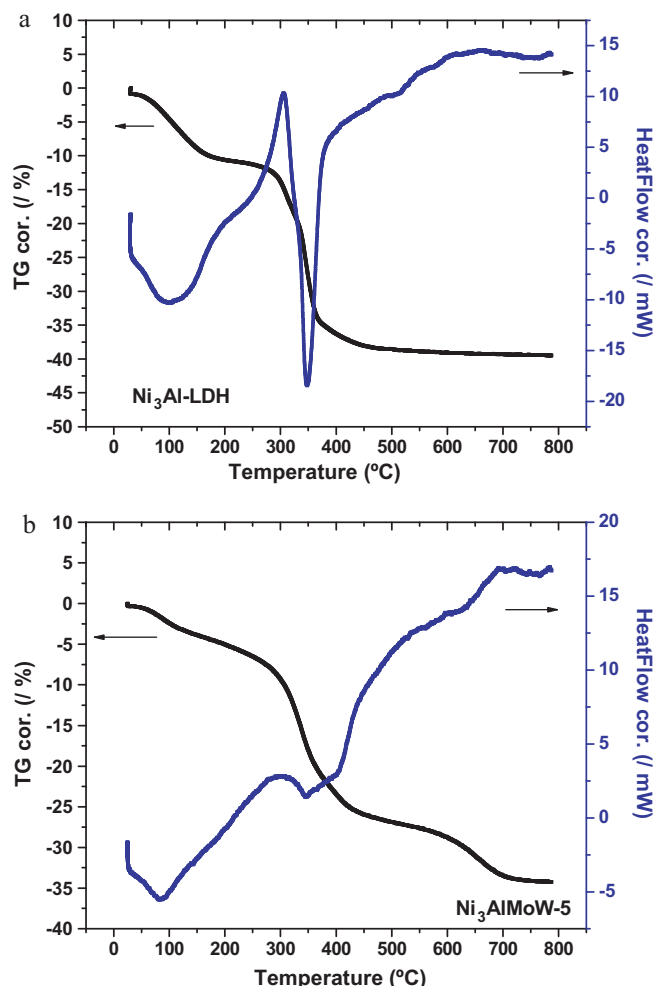**Fig. 2.** TG/DTG curves of the (a) Ni$_3$Al-LDH and (b) Ni$_3$AlMoW-5 catalysts.

two main endothermic peaks at about 100 °C and 350 °C: the first one corresponds to the removal of water, and the second one corresponds to the dehydroxylation of the LDH hosts as well as the destruction of the NO_3^- anions in the layers [33,34]. Accordingly, the DSC signal of Ni_3AlMoW-5 catalyst (Fig. 2(b)) also shows two main peaks besides the peak at 100 °C due to removal of water: one at about 350 °C corresponds to the decomposition of the Mo and W salts, dehydroxylation of the LDH hosts, and destruction of the NO_3^- anions in the layers; the other one at about 650 °C corresponds to the loss of oxygen by decomposition of the oxides, which is much lower than that reported in the literature, [35] indicating that our sample can easily lose its oxygen and exhibits higher activity. We supposed that the Mo and W species form a composite compound in the interlayer galleries as well as on the surface of the LDH. This kind of composite compound has higher HDS activity and readily loses its oxygen, resulting in the decrease of the decomposition temperature of these species.

4,6-Dimethyldibenzothiophene (4,6-DMDBT) in decalin was used as a model of sulfur-containing compound (sulfur content of 500 ppm), and the HDS performance of the Ni_mAl_nMoW-p and the commercial $CoNiMoW/Al_2O_3$ catalysts were evaluated under the same mild operating conditions. The experimental results are summarized in Table 1. It can be seen that the Ni_3AlMoW-p sulfide catalyst exhibits higher HDS activity than the commercial $CoNiMoW/Al_2O_3$ catalyst. The Ni_3AlMoW-5 catalyst even shows a specific HDS activity value about 5.6 times higher than that of the commercial catalyst. The sulfur content in the model compound could be reduced from 500 ppm to less than 20 ppm by this catalyst under this operation condition.

The effects of pH values in the ion exchange reaction on the properties of NiAlMoW catalysts were investigated. The XRD patterns
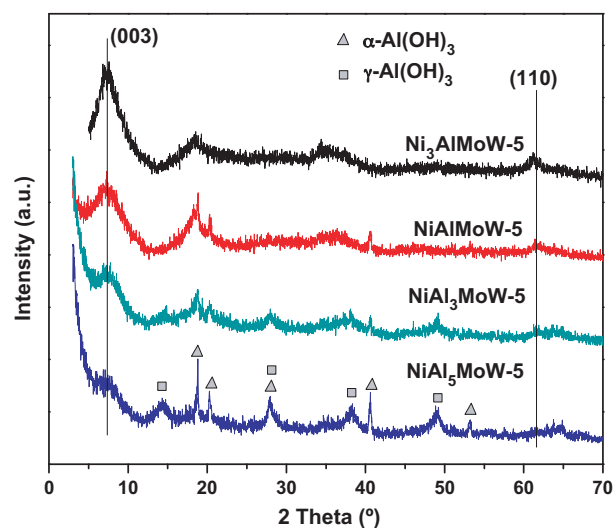

Fig. 3. XRD patterns of Ni_mAl_nMoW-5 precursors prepared by different Ni/Al molar ratios. The majority of the Al species were in the framework of NiAl-LDH, there were still a certain amount of the Al species that became non-framework $Al(OH)_3$ in the forms of α-$Al(OH)_3$ and γ-$Al(OH)_3$.

of the Ni_3AlMoW-p catalyst precursors prepared under different pH values of p are shown in Fig. 1. The peaks at ~10.5° due to (0 0 3) plane of LDH disappeared when the applied pH values were lower than 5, indicating that the Mo and W species were completely exchanged into the galleries of the NiAl-LDH layers. With the decrease of the pH value, the yields of the catalysts also decrease, and one could hardly obtain Ni_3AlMoW-p catalyst at pH = 1, imply-
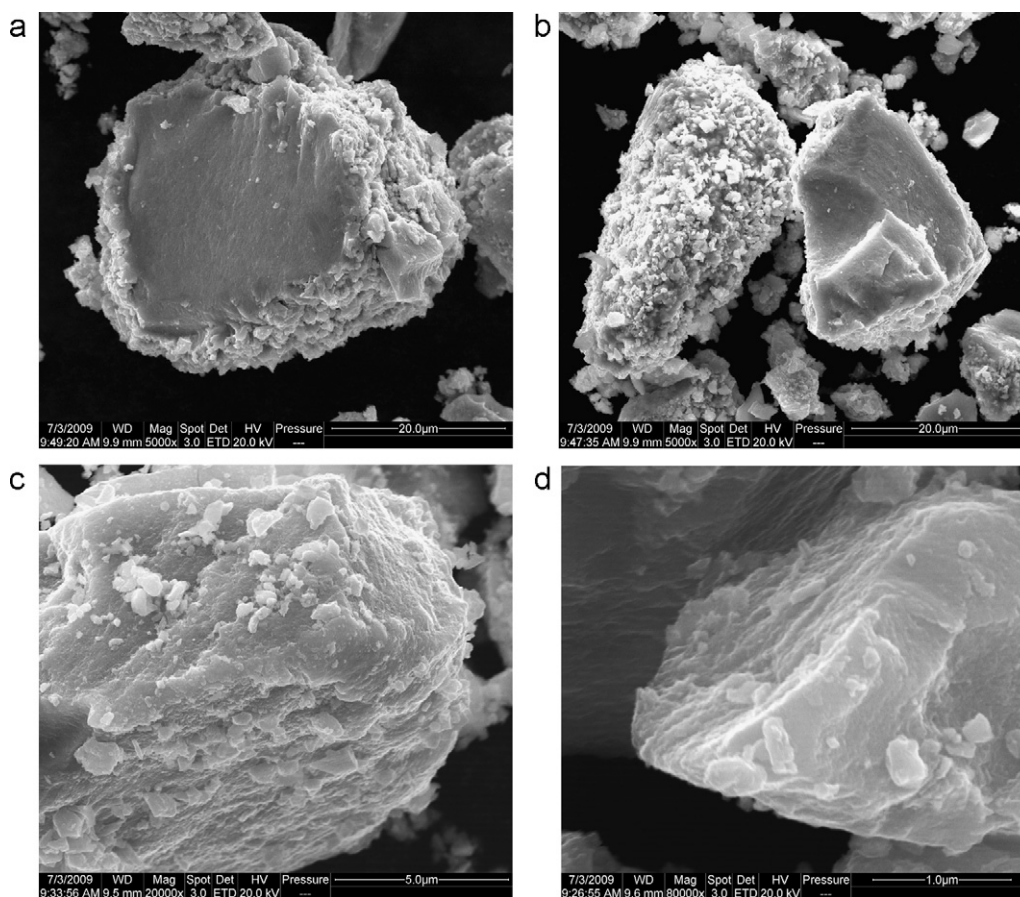

Fig. 4. SEM images of Ni_3AlMoW-5 sulfide catalysts (a and b) prepared in water and (c and d) prepared with EG and surfactant in solvent.
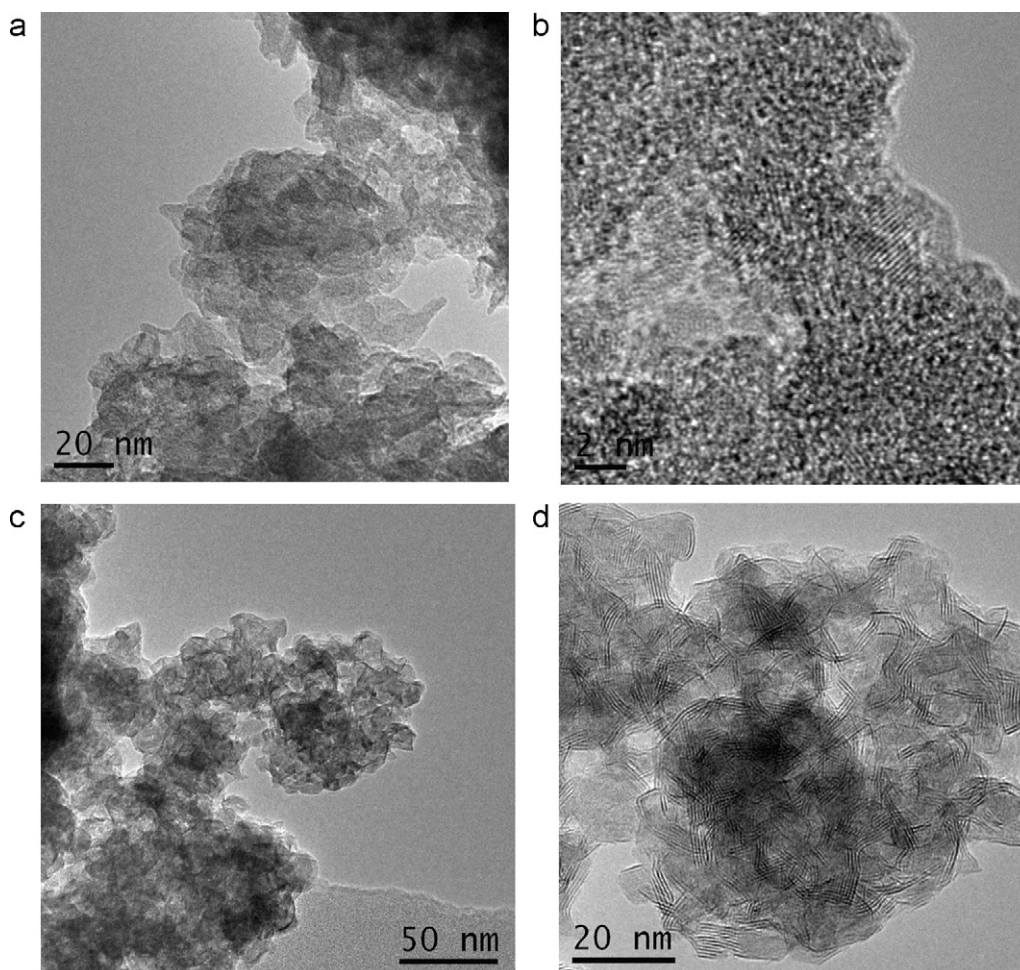
Fig. 5. HRTEM images of Ni₃AlMoW-5 catalyst precursor (a) at 20 nm scale and (b) at 2 nm scale; Ni₃AlMoW-5 sulfide catalyst at (c) 50 nm scale and (d) at 20 nm scale.

ing that the catalyst was destroyed under strong acidic conditions. This made us draw the conclusion that the pH values in the ion exchange reaction affect the HDS activities of the NiAlMoW catalysts and that the best pH value for the synthesis is at about pH = 5.

Table 1 shows the summarized data of physicochemical properties of the catalysts prepared at different pH values during ion exchange and corresponding HDS catalytic activities. The surface areas of these Ni₃AlMoW-p catalyst precursors were all about 100 m²/g, except that the Ni₃AlMoW-9 sample prepared in basic solution (pH = 9) has a larger surface area of about 147 m²/g. However, larger surface area does not result in high HDS activity, since the highest HDS activity of 568 is from Ni₃AlMoW-5 sample, which has a smaller surface area of 96 m²/g prepared at pH = 5. The pore size and pore volume came to the highest values with the pH of 7. The pore size could be comparable with that of the usual NiMo catalyst, while the pore volume is lower due to the absence of support. However, the pore properties of the NiAlMoW catalysts were better than those of the bulk NiMoW catalysts in the Ref. [22]. It should be noticed that the HDS activities changed with the pore size and pore volume. However, the pore properties of the catalyst were not the only reason for the high HDS activity. These results indicate that the physicochemical properties of the catalyst did not play a key role in the promotion of the HDS activity of the catalysts.

The effects of Ni/Al molar ratios on the HDS activities of NiAlMoW catalysts were also studied. A series of Ni$_m$Al$_n$MoW-5 catalysts with different Ni/Al ratios were synthesized at pH = 5 in the ion exchange process. Fig. 3 shows the XRD patterns of these catalysts. The characteristic diffraction peaks of (0 0 3) plane of the

NiAl-NO₃ LDH were observed at ~7.2° in all the catalysts, confirming the formation of layered structure. The shift of the (0 0 3) plane from ~10.5° in Ni$_m$Al$_n$-NO₃ LDH (not given in the XRD patterns) to the lower diffraction angle in Ni$_m$Al$_n$MoW-5 precursors is an indication of the successful ion exchange for $Mo_7O_{24}^{6-}$ and $H_2W_{12}O_{40}^{6-}$. It should noted that the diffraction peaks of (1 1 0) plane were weakened and some α-Al(OH)₃ and γ-Al(OH)₃ were formed in the catalysts when the Ni/Al ratio decreased. Researchers have suggested that the high content of Al metal in the NiAl-LDH led to the destruction of layered structure and that a certain amount of the Al species became Al(OH)₃ [36].

Table 2 shows the HDS activities and compositions of the Ni$_m$Al$_n$MoW-5 catalysts prepared with different Ni/Al ratios. It can be seen that the specific HDS activity of the catalysts for the 4,6-DMDBT model compound decreases with the addition of the Al, except for the NiAl₃MoW-5 catalyst. The calculated intrinsic HDS activities, i.e., the HDS activity of per unit weight of active metal in catalyst, were not changed linearly with the increase of the Al content in the catalysts. The Ni₃AlMoW-5 and NiAl₃MoW-5 catalysts exhibited higher intrinsic HDS activities than others, and even about 2 times higher than that of the commercial catalyst. Meanwhile, the active metal contents in the catalyst were reduced from 77.3% in NiMoW catalyst to 48.1% and 71.4% in NiAl₃MoW-5 and Ni₃AlMoW-5 catalysts, respectively. This implies that the active metal content was not the only reason for the high HDS activity of the catalyst. Combining with the results of XRD and the data listed in Table 1, we conclude that the layered structure of catalyst has more responsibilities for the improvement of the HDS activity.
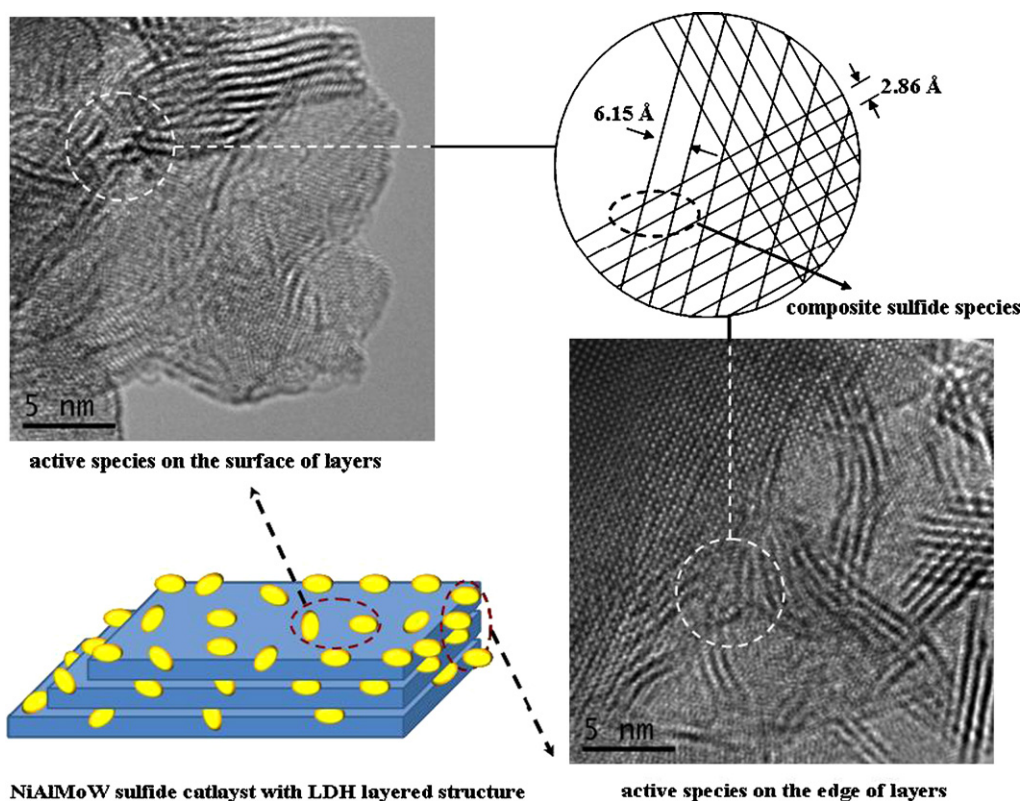
Fig. 6. HRTEM images and scheme of active species in Ni$_3$AlMoW-5 sulfide catalyst.

On the basis of the above conclusion, the active metal content in the catalyst could be reduced by adjusting the Ni/Al ratio in the preparation of the NiAl-LDH on the premise of reservation of the layered structure in catalyst, while maintaining the high intrinsic HDS activity for the unsupported NiMoW catalyst. Considering the high HDS activity and cost effectiveness, the NiAl$_3$MoW-5 catalyst might be an appropriate new generation HDS catalyst.

In order to further understand the effect of the morphology on the HDS activity, we applied SEM, TEM and HRTEM to character-ize the morphology of the catalysts. The SEM images (Fig. 4(c and d)) of the Ni$_3$AlMoW-5 sulfide catalyst show uniformly distributed nanoparticles on the surface of the layered structure. Considering the preparation process of the NiAlMoW catalysts, one can the par-ticles on the surface to the Mo, W and MoW composite species, while the layer sheet is the host layer of NiAl-LDH. As can be seen in the SEM images (Fig. 4(a and b)) of catalyst synthesized without ethylene glycol and surfactant, the particles were just agglom-erated on the surface of the LDH, preventing full promotion by the Ni species on the LDH. It should be noted that the numbers of particles on the surface of LDH are much more in the catalyst prepared with water than in the one prepared with ethylene glycol and surfactant. As the catalysts were prepared under the same experimental con-ditions by loading the same amount of active metals, it is supposed that only part of the Mo and W species were exchanged into the galleries of the LDH layers in the NiAlMoW catalysts when it was synthesized without using ethylene glycol and surfactant. Further-more, in the HDS of 4,6-DMDBT, the NiAlMoW catalyst prepared with ethylene glycol and surfactant exhibited higher activity than the catalyst prepared in water. The sulfur contents in the samples after HDS reaction were 18 ppm and 32 ppm, respectively. The spe-cific HDS activity for catalyst prepared with ethylene glycol and surfactant was about 1.6 times higher than that for the catalyst prepared in water. This demonstrates that introduction of surfac-tant and organic solvents like ethylene glycol in preparation could promote the dispersion of the active species on the surface as well as on the internal surface of the LDH layers. High dispersion of the active species surely will lead to excellent HDS performance of the catalyst.

The HRTEM images of Ni$_3$AlMoW-5 catalyst precursor (Fig. 5(a and b)) and corresponding sulfide catalyst (Fig. 5(c and d)) show that they both are comprised of small sheets, stacked irregularly. After sulfidation of the precursor, the sulfide catalyst exhibits the fringes with characteristic basal spacing of 2.86 Å due to NiS species and some crystal lattices of Al$_2$O$_3$ covered by the curved slabs of WS$_2$ and MoS$_2$ with the basal spacing of 6.15 Å. Overall, the HRTEM images clearly show that the WS$_2$ and MoS$_2$ species were well dis-persed in the catalysts with the average slab length of 3–10 nm and the stacking number of 2–6 slabs.

HRTEM images in Fig. 6 further reveal that there are mainly two locations for the active species in the sulfide catalyst. Some of the active species are located on the surface of the LDH layers, while the others are located on the edge of the layers. It was reported that the HDS active sites were mainly at the curvature of the basal planes and the edge planes of the active metal sulfide [37,38]. In this catalyst, the MoS$_2$, WS$_2$ or Mo$_x$W$_{1-x}$ species contact well with NiS species, and some composite sulfide species are formed both on the plane surface and edge sites. The active species on the edge sites of layers could enhance the interaction among the WS$_2$, MoS$_2$ and Mo$_x$W$_{1-x}$S$_2$ by Ni atoms, resulting in the formation of more Ni–Mo–S, Ni–W–S and Ni–Mo–W–S active sites.

Based on the XRD, SEM and HRTEM results, the model of the NiAlMoW catalyst and the processes for the formation of sulfide NiAlMoW catalyst can be depicted as shown in Fig. 7. The NiAlMoW catalyst exhibits a multi-layered structure retained from the NiAl-NO$_3$ LDH material, which could lead to better interaction among the active metal sulfide compounds. The active species are uniformly dispersed on both the surface and the edge sites of the NiAl-LDH layer, leading to excellent HDS performance.
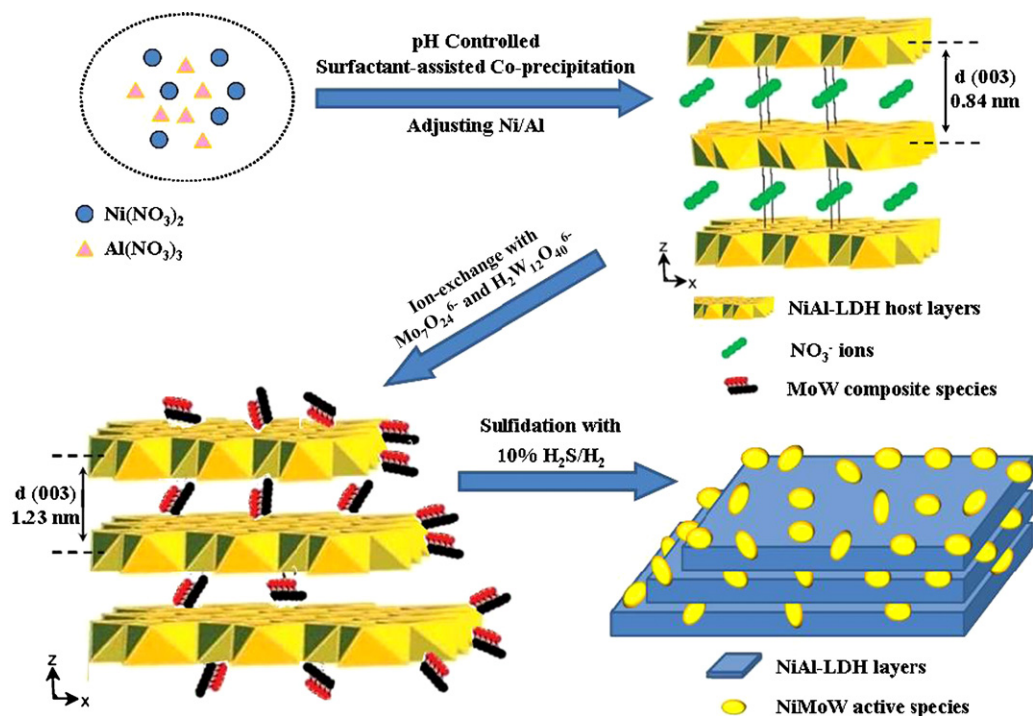
Fig. 7. Schematics showing the formation of sulfide NiAlMoW catalyst with LDH structure.

4. Conclusion

In conclusion, the NiAlMoW catalyst has been prepared using NiAl-LDH as structure-directing template. These catalysts exhibit high catalytic activities in the HDS of 4,6-DMDBT. The NiAl$_3$MoW-5 catalyst shows about 2 times higher HDS intrinsic activity than commercial catalyst. Meanwhile, the active metal contents in the catalyst were reduced from 77.3% in NiMoW catalyst to 48.1% in NiAl$_3$MoW-5 catalyst, respectively. After series characterizations, we found that the NiAlMoW catalyst maintained the multi-layered structure of the NiAl-LDH precursor. Furthermore, it is found that the layered structure of the catalyst is beneficial for the improvement of the dispersion of active species and HDS activity. Thus, the novel catalyst with high HDS activity can be designed and prepared by surfactant-assisted co-precipitation method using NiAl-layered double hydroxide (NiAl-LDH) as the structure-directing template.

Acknowledgement

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