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Mesoporous zeolite-supported metal sulfide catalysts with high activities in the deep hydrogenation of phenanthrene



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ABSTRACT

Developing highly active hydrogenation catalysts for deep aromatics saturation is of great importance in the production of ultraclean diesel fuel at a low cost. Toward this goal, we synthesized a mesoporous zeolite ZSM-5 (MZSM-5) that was cost-effective and available on a large scale, and used it as a support for the preparation of highly efficient metal sulfide catalysts (NiMoS/MZSM-5 and CoMoS/MZSM-5) for the deep hydrogenation of phenanthrene. The intrinsic activity of the NiMoS/MZSM-5 catalyst ($7.4 \times 10^{-4} \text{ mol kg}^{-1} \text{ s}^{-1}$) was much higher than that of the alumina-supported NiMo catalyst (NiMoS/ γ -Al₂O₃, 4.8 × 10⁻⁴ mol kg⁻¹ s⁻¹), and the selectivity of the deep hydrogenation products over NiMoS/MZSM-5 (20.9%) was higher than for NiMoS/ γ -Al₂O₃ (15.2%). Compared with γ -Al₂O₃, the relatively weak metal–support interaction could facilitate the formation of polymolybdates on MZSM-5. After sulfidation, the more multistacked MoS₂ active phases were formed on the MZSM-5, enhancing the hydrogenation activity of the NiMoS/MZSM-5 catalyst.

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1. Introduction

The high aromatic content in diesel fuel lowers the fuel quality and contributes to the formation of undesirable emissions in exhaust gases [1–5]. A solution to this problem is to saturate the aromatics by hydrogenation over conventional γ -Al₂O₃-supported metal sulfide catalysts (CoMoS/ γ -Al₂O₃ and NiMoS/ γ -Al₂O₃) [5–10]. However, the deep saturation of aromatics over these types of catalysts is difficult because of their low catalytic activities [2,11]. Because aromatic hydrogenation is an exothermic and reversible reaction, catalysts with high activities at low temperature and pressure could benefit deep hydrogenation. Extensive studies show that noble metal catalysts such as Pd. Pt. and Pd-Pt have high activities [12–14], but they are fairly sensitive to sulfur and nitrogen compounds, severely limiting their practical applications [15–18]. Therefore, developing highly active catalysts with good sulfur resistance for the deep hydrogenation of aromatics at low temperature and pressure is of great importance for the cost-effective production of clean diesel fuel.

The hydrogenation activity of supported metal catalysts is greatly influenced by the nature of the support, such as its acidity [19–23], surface area [24–26], and pore structure [27–29]. For instance, the activity of a metal sulfide supported on γ -Al₂O₃ can be enhanced through addition of additives (F, P, and B as well as acidic zeolite) to the support by modifying the acidity of the catalyst or increasing the metal dispersion [19-23]. However, the deep hydrogenation of aromatics remains a challenge. Ordered mesoporous molecular sieves with high surface area and mesopore volume, such as MCM-41 and SBA-15, were used as supports of metal sulfide catalysts to increasing the metal dispersion and mass transfer, resulting in high catalytic activity [26,30,31]. However, the relatively lower hydrothermal stability of this type of material severely limits its industrial applications [13,30]. Crystalline zeolites with unique porous structures and modifiable surface properties are widely used in oil and gas processing [32]. For example, metal sulfide clusters (MoS_x) dispersed inside the micropores of zeolite Y and ZSM-5 have high activity in toluene hydrogenation and hydrodesulfurization of dibenzothiophene [33,34]. Nevertheless, conventional zeolites cannot accomplish deep hydrogenation of the polyaromatic hydrocarbons due to their pore size limitation [35–37]. Recently, mesoporous zeolites with excellent catalytic activity for the conversion of bulky molecules have been successfully synthesized [38-46]. In particular, metal sulfide catalysts (CoMoS₂ and NiMoS₂) supported on mesostructured zeolite nanofiber assemblies show unprecedented hydrodesulfurization activity in the deep hydrodesulfurization (HDS) of the bulky



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4,6-dimethyldibenzothiophene [47]. As an extension of this work, we report here a facile method for synthesizing mesoporous ZSM-5 (MZSM-5) at low cost at a large scale. After loading nickel (or cobalt) and molybdenum, followed by sulfidation, the MZSM-5-supported metal sulfide catalysts (NiMoS/MZSM-5 and CoMoS/MZSM-5) exhibit high activity in the deep hydrogenation of bulky aromatic phenanthrene under mild conditions (280 °C and 5 MPa), as compared with conventional NiMoS/ γ -Al₂O₃ and Pd catalysts supported on MZSM-5 (Pd/MZSM-5). This work provides a new opportunity for the preparation of series of highly active hydrogenation catalysts for the deep saturation of polyaromatics. This is of great significance for increasing fuel quality and controlling undesirable emissions in exhaust gases.

2. Experimental

2.1. Material synthesis

MZSM-5 was synthesized hydrothermally from an aluminosilicate gel with a molar composition of Al₂O₃/50SiO₂/16.2Na₂O/ 0.015RCC/1490H₂O, where RCC was a random cationic copolymer that contained quaternary ammonium groups and was synthesized using cheap starting materials [47]. In a typical run, 20.4 L of water glass was mixed with 23.2 L NaOH aqueous solution (2.1 wt.%) followed by 3.0 L RCC. After stirring at room temperature for 2 h, 22.2 L acidic $Al_2(SO_4)_3$ aqueous solution (3.7 wt.%) was added. The mixture was further stirred for 2 h to yield an aluminosilicate gel. The gel was transferred into a stainless steel autoclave (100 L) for dynamic crystallization at 170 °C for 3 days. After filtration and washing, the sample was dried at 120 °C overnight and calcined in air at 550 °C for 5 h. Mesopore-free ZSM-5 was synthesized by the same procedure except for the absence of RCC. Nanofiber bundles of mordenite (NB-MOR) with mesoporous structure were synthesized according to a previous work [47].

2.2. Catalyst preparation and pretreatment

The NiMo catalysts were prepared by an incipient wetness impregnation method using an ammonia solution containing required amounts of ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O), nickel nitrate (Ni(NO₃)₂·6H₂O), and ethylenediaminetetraacetic acid (EDTA). The molar ratio of Ni/Mo/EDTA was 1:2:1 and the Mo loading was 12.0 wt.%. The pH value of the impregnation solution was about 11. MZSM-5, ZSM-5, NB-MOR, and γ -Al₂O₃ in powder form were used as supports to prepare the catalysts. After impregnation, the sample was dried under ambient conditions for 20 h and subsequently dried at 120 °C for 12 h without calcination. The dried powder catalyst sample was tableted (15 MPa) and crushed and sieved to form 40-60 mesh particles. The dried particle sample was directly presulfided in a gas mixture of H_2-H_2S (10 vol.% H_2S) from room temperature to 400 °C at a heating rate of 2 °C min⁻¹ and kept for 3 h at 400 °C before catalytic testing. The dried catalysts with MZSM-5, ZSM-5, NB-MOR and γ -Al₂O₃ supports were designated as NiMo/MZSM-5, NiMo/ZSM-5, NiMo/NB-MOR, and NiMo/y-Al2O3, respectively. Correspondingly, the sulfided catalysts were designated as NiMoS/ MZSM-5, NiMoS/ZSM-5, NiMoS/NB-MOR, and NiMoS/γ-Al₂O₃, respectively. To investigate the relationship between the active phase morphology and the hydrogenation activity on the MZSM-5-supported NiMo catalysts, the catalysts with different Mo loadings (3.0 and 6.0 wt.%) were prepared by the same procedure, and the sulfided catalysts were designated as NiMoS/MZSM-5-L and NiMoS/MZSM-5-I. MZSM-5-, NB-MOR-, and γ -Al₂O₃-supported CoMo catalysts were prepared similarly. The sulfided catalysts were designated as CoMoS/MZSM-5,

CoMoS/NB-MOR, and CoMoS/ γ -Al₂O₃. The molar ratio of Co/Mo/ EDTA was 1:2:1 and the Mo loading was 12.0 wt.%. MZSM-5- and γ -Al₂O₃-supported Ni (3.7 wt.%) and Mo (12.0 wt.%) catalysts were prepared in the same way.

MZSM-5-supported Pd catalyst (Pd/MZSM-5) was prepared by incipient wetness impregnation of MZSM-5 with an aqueous solution of $[Pd(NH_3)_4]Cl_2$. After impregnation, the sample was dried in air at ambient temperature for 20 h and further dried at 120 °C for 12 h. The dried sample was finally calcined at 450 °C for 4 h. The Pd loading of this catalyst was 3.0 wt.%.

2.3. Characterization

An X-ray diffraction (XRD) pattern was obtained with a RIGAKU UltimalV diffractometer using Cu K α radiation. Nitrogen physisorption was conducted at -196 °C on a Micromeritics ASAP 2020 M apparatus. The sample was degassed for 8 h at 300 °C before the measurement. Specific surface area was calculated from the adsorption data using the Brunauer-Emmett-Teller (BET) equation. The pore size distribution was calculated according to the Barrett-Joyner-Halenda (BJH) model using adsorption data. Fourier transform infrared spectroscopy (FT-IR) of the MZSM-5 sample was performed on a Bruker TENSOR 27 equipped with a reactor cell. To investigate the surface properties of the MZSM-5, the sample was outgassed overnight at 450 °C and 7.5 Pa before IR measurement. Thermogravimetric (TG) analyses of the fresh and spent catalysts were carried out from 40 to 900 °C at 10 °C min⁻¹ under flowing air (20 mL min⁻¹) on a STA6000 instrument. For the spent catalysts, the sample was thoroughly washed with ethanol and dried at 60 °C for 12 h before TG analysis. The acidity of the sulfided catalysts was measured using stepwise temperature-programmed desorption of ammonia (NH₃-STPD) on a Micromeritics ASAP2920 instrument. A 200-mg sample was placed in a quartz tube and pretreated in a helium stream at 450 °C for 2 h. After the sample was cooled to 120 °C, NH₃-He mixed gas (10 vol.% NH₃) was passed over the sample for 30 min. After removal of the physically adsorbed NH₃ by flowing helium for 2 h at 120 °C, the sample was treated as follows: (1) increasing the temperature from 120 to 180 °C at a rate of 10 °C min⁻¹ and holding at 180 °C for 30 min, (2) increasing the temperature from 180 to 250 °C at a rate of 10 °C min⁻¹ and holding at 250 °C for 30 min, (3) increasing the temperature from 250 to 300 °C at a rate of 10 °C min⁻¹ and holding at 350 °C for 30 min, and (4) increasing the temperature from 350 to 800 °C at a rate of 10 °C min⁻¹ and holding at 800 °C for 30 min. The desorbed NH₃ was collected in dilute hydrochloric acid and titrated with a dilute sodium hydroxide solution to determine the acidic site density of the samples. Temperature-programmed reduction (TPR) of the dried catalysts was also conducted on a Micromeritics ASAP2920 instrument equipped with a cold trap (-80 °C, filled with a mixture of isopropanol and liquid nitrogen) that was installed in front of the TCD entrance. Thus, the products caused by decomposition of the EDTA and metal precursor in the sample could be trapped in the cold trap (discussed in the Supporting Information; see Fig. S1). A dried sample (50 mg) was placed in a quartz tube and heated to 1000 °C at 15 °C min⁻¹ in a H₂-Ar (10 vol.% H₂) gas mixture stream.

The UV–vis diffuse reflectance spectra (UV–vis DRS) were obtained on a Perkin-Elmer Lambda25 spectrometer with an integration sphere. The Raman spectra were measured with a Renishaw Raman 2000 microprobe (532 nm laser excitation). X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB MK II system. Before analysis, the dried catalyst was sulfided in mixed H_2S-H_2 gas with 10% H_2S (60 mL min⁻¹, STP) at 400 °C for 180 min. After sulfidation, the catalyst was purged by He (99.999%, 80 mL min⁻¹) at 400 °C for 60 min. After cooling to room temperature, the sulfided catalyst was transferred under a helium

stream into a bottle filled with absolute cyclohexane. For XPS experiments, the cyclohexane in the bottle was removed and the residual sulfided catalyst was quickly moved to a sample holder and then transferred into an analysis chamber in the XPS instrument. For comparison, the spent catalysts were also analyzed by XPS.

The morphology of the MZSM-5 sample was observed with a field emission scanning electron microscope (SEM) on a SUPRA55 apparatus operated at an accelerating voltage of 5 kV. The sample was coated with gold to create contrast. The transmission electron microscopy (TEM) image was obtained on a JEM-2100F microscope with a limited line resolution capacity of 1.4 Å at 200 kV. Before characterization by TEM, the samples were cut into thin slices and dropped onto a Cu grid coated with carbon membrane. Typically, at least 40 TEM micrographs were measured for the sulfided NiMo catalysts supported on MZSM-5 and γ -Al₂O₃, including 400– 500 slabs taken from different parts of each catalyst. To measure the MoS_2 dispersion (f_{Mo}), which is defined as the average fraction of Mo atoms at the MoS_2 edge surface, we assumed that the MoS_2 slabs are present as perfect hexagons. The f_{Mo} was calculated by dividing the total number of Mo atoms at the edge surface by the total number of Mo atoms using the slab sizes determined from the TEM micrographs [48],

$$f_{Mo} = \sum_{i=1,\dots,t} (6n_i - 6) / \sum_{i=1,\dots,t} (3n_i^2 - 3n_i + 1)$$

where n_i is the number of Mo atoms along one edge of a MoS₂ slab determined from its length ($L = 3.2(2n_i - 1)$ Å), and t is the total number of slabs shown in the TEM micrographs. The average slab length (\overline{L}) and stacking layer number (\overline{N}) were calculated according to the equations [49,50]

$$\overline{L} = \frac{\sum_{i=1}^{n} x_i L_i}{\sum_{i=1}^{n} x_i}$$

$$\overline{N} = \frac{\sum_{i=1}^{n} y_i N_i}{\sum_{i=1}^{n} y_i}$$

where L_i is the length of slab *i*, N_i is the number of layers in slab *i*, x_i is the number of slabs with length L_i , and y_i is the number of slabs with N_i layers.

2.4. Activity tests

The phenanthrene (PHE) hydrogenation was carried out in a fixed-bed continuous-flow stainless steel reactor (internal diameter 6.5 mm and length 500 mm). A sample of 0.2 g presulfided catalyst was diluted with 1.5 g SiC before being loaded into the reactor. Both ends of the catalyst bed were filled with extra 0.3 g SiC. The calcined Pd catalyst was pretreated in situ with flowing H₂ (40 mL min⁻¹) at 300 °C for 2 h before catalytic testing. The operating conditions were as follows: total pressure of 5.0 MPa, temperature of 280 °C, 0.6 wt.% phenanthrene, and 0.1 wt.% dimethyldisulfide (795 ppm of sulfur) in decalin. The weight hourly space velocity of the feed solution was 14.0 h⁻¹, and the H₂/oil ratio was 1125 Nm³/m³. The products were collected and analyzed using an Agilent 7890A GC installed with a FID detector. The products were further analyzed with a mass spectrometer (SHIMADZU GCMS-QP2010).

To investigate the intrinsic hydrogenation activity of the catalysts, the mass transfer and heat transfer effect can be ruled out using the Weisz–Prater criterion and a Mears criterion [51]. The experimental test used a desired amount presulfided catalyst (60–80 mesh, containing 62.5 μ mol Mo) diluted with 1.8 g SiC (40–60 mesh) that was loaded into the reactor. After the reaction was stable, the phenanthrene conversion was kept a low level by changing the weight hourly space velocity. The internal and

external diffusion limitations were checked by the Weisz–Prater criterion (C_{WP}) and the Mears criterion (C_M) [51], respectively:

$$C_{WP} = \frac{r_{obs}\rho_c R_p^2}{D_{eff}C_s},$$
$$C_M = \frac{r_{obs}\rho_b R_P n}{k_c C_m},$$

_1

where r_{obs} is the observed reaction rate, mol kg⁻¹ s⁻¹; *n* is the reaction order; R_P is the catalyst particle radius, m; ρ_c is the bulk density of the catalyst bed, kg m⁻³; ρ_b is the bulk density of the catalyst bed, kg m⁻³, $\rho_b = (1 - \varepsilon)\rho_c$; ε is porosity; C_s is the bulk concentration of phenanthrene at the external surface of the catalyst, mol m⁻³; C_{Ab} is the bulk concentration of phenanthrene, mol m⁻³; and k_c is the external mass transfer coefficient, m s⁻¹.

The heat transfer resistance was checked by the Mears criterion [51],

$$C_{MH} = \left| \frac{-\Delta H r_{obs} \rho_b R_p E}{h_p T^2 R_g} \right|,$$

where $\triangle H$ is the heat of reaction, kJ mol⁻¹; *E* is the activation energy, kJ mol⁻¹; *h* is the heat transfer coefficient between gas and pellet, kJ m⁻² s⁻¹ k⁻¹; *R*_g is the gas constant, kJ mol⁻¹ K⁻¹; and *T* is the reaction temperature, K.

The values for C_{WP} , C_M and C_{MH} were 0.001, 0.0036, and 6.5×10^{-7} under experimental conditions (see the Supporting Information). In general, the internal and external diffusion limitations and the heat transfer effect can be neglected during the kinetic experiments when the values of C_{WP} , C_M and C_{MH} are below 1, 0.15, and 0.15, respectively. Thus, in our case, the internal and external diffusion limitations and the heat transfer effect could be neglected during the kinetic experiments. In this case, the observed reaction rate (r_{obs}) can be used to assess the intrinsic hydrogenation activity of the catalysts. r_{obs} was calculated as [52]

$$r_{obs} = \frac{dx}{d(W/F)}$$

where *F* is the reactant molar flow (mol s^{-1}), *x* is the phenanthrene conversion (%), and *W* is the catalyst mass (kg).

The phenanthrene hydrogenation turnover frequencies (TOF, $s^{-1})$ were calculated according to the equation $\left[48\right]$

$$TOF = \frac{F \times x}{N_{Mo} \times f_{Mo}},$$

where x is the phenanthrene conversion (%), N_{Mo} is the number of Mo atoms in the catalyst (mol), and f_{Mo} is the MoS₂ dispersion.

3. Results and discussion

3.1. Characterization

Fig. 1 shows the XRD patterns of the supports and catalysts. The MZSM-5 sample exhibits typical peaks in the range of $5-50^{\circ}$ associated with the MFI structure. After impregnation of the MZSM-5 with nickel and molybdenum, followed by drying and sulfidation, the intensity of the diffraction peaks in the samples is slightly weakened, whereas the MFI structure in the samples is maintained. No other crystalline phases (MoO₃ or β -NiMoO₄) are detected in the NiMo/MZSM-5 and NiMoS/MZSM-5 catalysts, indicating that the Ni and Mo species are well dispersed in both dried and sulfided catalysts. Notably, there is no change in the peak position for the spent NiMoS/MZSM-5 catalyst, demonstrating that the MFI structure in the catalyst is retained after hydrotreating.



Fig. 1. XRD patterns of (a) MZSM-5, (b) NiMo/MZSM-5, (c) NiMoS/MZSM-5, and (d) spent NiMoS/MZSM-5 samples.



Fig. 2. Nitrogen adsorption–desorption isotherms and pore size distributions of the (a) MZSM-5 and (b) γ -Al₂O₃ samples in powder form. (The isotherm of γ -Al₂O₃ has been offset by 60 cm³ g⁻¹ along the vertical axis for clarity. The pore size distribution of γ -Al₂O₃ has been offset by 0.24 cm³ g⁻¹along the vertical axis for clarity.).

Fig. 2 shows the N₂ adsorption-desorption isotherms and pore size distributions of the MZSM-5 and γ -Al₂O₃ samples in powder form. The isotherms present a hysteresis loop, indicating that the MZSM-5 and γ -Al₂O₃ samples contain a mesoporous structure. Correspondingly, the pore sizes of the two samples are centered at 22 and 8.1 nm. Because the catalyst was fashioned at a high pressure of 15 MPa before activity testing, to compare the change in the texture parameters of the support with the fashioned catalyst in the same way, N2 adsorption of the fashioned supports and catalysts was performed, and the results are shown in Figs. 3 and 4, respectively. Sample texture parameters of the supports and corresponding catalysts are presented in Table 1. Clearly, when the powder supports were transformed into fashioned forms, the mesopore volume and pore size decreased due to the extruding effect on the powder sample. After loading of metals and sulfidation, the mesopores were still presented in the catalyst samples (Fig. 4), but the BET surface area, mesopore volume, and pore size dimensions decreased further (inset in Fig. 4 and Table 1) due to the metal filling in the pores.

The SEM image reveals that the MZSM-5 particles have an "olive" morphology with particle sizes of 0.5 \times 1.5 μm (Fig. 5a). The TEM image of the thin-sectioned MZSM-5 gives direct evidence for the presence of abundant hierarchical mesopores in the crystals (Fig. 5b, light areas). The size range of the mesopores is in good agreement with that obtained from N₂ sorption (Fig. 2a, insert).



Fig. 3. Nitrogen adsorption–desorption isotherms and pore size distributions of (a) MZSM-5 and (b) γ -Al₂O₃ in fashioned form. (The isotherm of γ -Al₂O₃ has been offset by 70 cm³ g⁻¹ along the vertical axis for clarity. The pore size distribution of γ -Al₂O₃ has been offset by 0.24 cm³ g⁻¹ along the vertical axis for clarity.).



Fig. 4. Nitrogen adsorption–desorption isotherms and pore size distributions of (a) NiMoS/MZSM-5 and (b) NiMoS/ γ -Al₂O₃ catalysts. (The isotherm of NiMoS/ γ -Al₂O₃ has been offset by 50 cm³ g⁻¹ along the vertical axis for clarity. The pore size distribution of NiMoS/ γ -Al₂O₃ has been offset by 0.1 cm³ g⁻¹ along the vertical axis for clarity.).

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Texture parameters	of the supports and catalysts.	

Sample	$\frac{S_{BET}}{(m^2 g^{-1})^a}$	V_{micro} $(cm^3 g^{-1})^b$	V_{meso} $(cm^3 g^{-1})^c$	$\frac{S_{mic}}{(m^2 g^{-1})^d}$	$\frac{S_{ext}}{(m^2 g^{-1})^e}$
MZSM-5 ^f	360	0.08	0.30	185	175
γ -Al ₂ O ₃ ^f	322	-	0.45	-	322
ZSM-5 ^f	315	0.10	0.06	245	67
Tableted MZSM-5 ^g	347	0.08	0.21	192	155
Tableted γ -Al ₂ O ₃ ^g	303	-	0.35	-	303
Tableted ZSM-5 ^g	309	0.10	0.06	250	59
NiMoS/MZSM-5	236	0.05	0.14	127	109
$NiMoS/\gamma-Al_2O_3$	230	-	0.25	16	213
NiMoS/ZSM-5	217	0.07	0.04	177	40

^a BET surface area.

 $^{\rm b}$ Microporous pore volume, obtained from *t*-plot method.

^c Mesoporous pore volume, obtained from BJH adsorption cumulative volume of pores between 1.7 and 300 nm diameter.

^d Micropore surface area.

^e External surface area, obtained from *t*-plot method.

 $^{\rm f}$ The sample was in powder form, and $\gamma\text{-Al}_2\text{O}_3$ was purchased from Shanghai HENGYE Chemical Industry Co., Ltd.

^g The sample was tableted under a pressure of 15 MPa before N₂ physisorption.



Fig. 5. (a) SEM image of the MZSM-5 sample and (b) TEM image of the thinsectioned MZSM-5 sample.



Fig. 6. NH₃-STPD profiles of (a) NiMoS/MZSM-5 and (b) NiMoS/ γ -Al₂O₃ catalysts.

Fig. 6 shows the NH₃-STPD profiles of the NiMoS/MZSM-5 and NiMoS/ γ -Al₂O₃ catalysts. Generally, the acidity of the catalyst is classified as weak acidic (120–180 °C), medium weak acidic (180–250 °C), medium strong acidic (250–350 °C), and strong acidic (>350 °C) sites according to the desorption temperature of the adsorbed ammonia [29]. The acid–base titration results are presented in Table 2. It can be seen that the acidic site density on the NiMoS/ γ -Al₂O₃ sample is slightly higher than that on the NiMoS/MZSM-5 across all studied desorption temperatures (Fig. 6). To further investigate the acidity of the NiMoS/ γ -Al₂O₃ and NiMoS/MZSM-5 catalysts in the high desorption temperature range of 350–800 °C, He-STPD of the two catalyst samples was performed (Fig. S2 in the Supporting Information). Clearly, the profiles of the two catalysts in the range of 350–800 °C are still present.

Table 2

Total acidity and acidic site distribution of the NiMoS/MZSM-5 and NiMoS/ γ -Al_2O_3 catalysts.

Catalyst	Acidic amounts of the catalysts (μ mol g ⁻¹)							
	120-180 °C	180–250 °C	250-350 °C	>350 °C	Total			
NiMoS/MZSM-5	90	110	120	47	367			
NiMoS/γ-Al ₂ O ₃	111	140	145	-	396			



Fig. 7. UV-vis DR spectra of (a) NiMo/MZSM-5 and (b) NiMo/ γ -Al₂O₃ samples.

These results indicate that the area of the desorption profile in the high-temperature region is not completely induced by the adsorbed NH₃. The acid–base titration results also demonstrate that the strongly acidic sites on the NiMoS/MZSM-5 catalyst are only 47 μ mol g⁻¹, while there are no strongly acidic sites on NiMoS/ γ -Al₂O₃ (Table 2).

UV-vis analysis was performed to obtain the coordination state of the Mo species on the dried catalysts (Fig. 7). Generally, the absorption band at 230-260 nm is attributed to the isolated molybdate species in tetrahedral coordination, whereas the band at 270-330 nm is characteristic of polymeric octahedral Mo species [31,53]. In our case, the absorption band around at 250 nm for NiMo/ γ -Al₂O₃ and the band around at 300 nm for NiMo/MZSM-5 are observed, which indicate that the Mo species on γ -Al₂O₃ are mainly present in the form of tetrahedral Mo, while the polymeric octahedral Mo species are prominent on MZSM-5. These results suggest that the proportion of octahedral Mo species on MZSM-5 is higher than that on γ -Al₂O₃ support. The octahedral Mo species could interact weakly with the MZSM-5 support. This makes them easily reduced to more multistacked MoS₂ active phases, enhancing the hydrogenation activity of the NiMoS/MZSM-5.

The Raman analysis experiments were performed to further investigate the differences in the state of the Mo species on the MZSM-5 and γ -Al₂O₃ supports. This could be beneficial for a better understanding of the metal-support interaction. The band centered at approximately 950 cm⁻¹ for the two catalysts is ascribed to the symmetric stretching of the Mo=O bond in the polymolybdates $(Mo_7O_{24}^{6-} \text{ and } Mo_8O_{24}^{4-})$ [54–56] (Fig. 8). The polymolybdates are considered to interact weakly with the support, resulting in higher reducibility and activity during the hydrogenation reaction [54,56]. However, a shoulder band is observed at 895 cm⁻¹ on the NiMo/ γ -Al₂O₃ that can be attributed to the Mo=O stretching mode of the isolated MoO₄²⁻ with distorted tetrahedral symmetry [55,57]. This Mo species present relatively low reducibility during the catalyst sulfidation due to the strong interaction of the Mo with the γ -Al₂O₃ via Mo–O–Al bridges [50,58]. In contrast, the band at 895 cm⁻¹ is not observed on the NiMo/MZSM-5 sample, while the



Fig. 8. Raman spectra of (a) NiMo/MZSM-5 and (b) NiMo/γ-Al₂O₃ samples.

bands at 993, 818, 335, and 281 cm^{-1} are detected for the NiMo/MZSM-5 sample, which could be induced by "free" MoO₃ crystallites composed of octahedral MoO₆ [59]. It has been reported that the "free" MoO₃ crystallites can be formed on the silica [60], which is due to the weaker interaction between the metal and surface hydroxyl on the support [57,60–62]. In our case, IR analysis shows that the acidic hydroxyl and silica hydroxyl groups exist on the MZSM-5 [63] (Fig. S3 in the Supporting Information), which results in relatively weak metal–support interaction, leading to formation of easily reducible "free" MoO₃ and polymolybdates in the NiMo/MZSM-5 catalyst.

To investigate the reduction behavior of Mo and Ni species in the catalyst precursors, TPR of the Ni, Mo, and NiMo catalysts supported on MZSM-5 and γ -Al₂O₃ was carried out, and the results are shown in Figs. 9 and 10. For the Ni/MZSM-5 sample (Fig. 9a), the overlapping profiles in the temperature range of 367–690 °C can be assigned to the reduction of Ni²⁺ and Ni octahedral species (Ni_{oct}^{2+}) [64,65]. The very small profiles with peak at 210 °C may be associated with the superficial reduction of nickel oxide [66]. For the Mo/MZSM-5 sample (Fig. 9b), the reduction profile with peak at 445 °C is assigned to the reduction of the octahedral Mo species $(Mo^{6+} + 2e^- \rightarrow Mo^{4+})$ in weak interaction with the MZSM-5 support; the profile with peak at 578 °C is assigned to the further reduction of the octahedral Mo species (Mo⁴⁺ + 4e⁻ \rightarrow Mo⁰) [53,67]. Compared with the reduction behavior of the Mo/MZSM-5 and Ni/MZSM-5 samples, the profile with a peak at 370 °C should involve the reduction of octahedral Mo and Ni²⁺ species, and the profile with a peak at 561 °C should be attributed to the further reduction of the octahedral Mo species and Ni_{oct}²⁺ species for the NiMo/MZSM-5 sample (Fig. 9c) [53,64,65]. Similarly, the reduction profile in the relatively low temperature range of 325-625 °C is also observed on the NiMo/ γ -Al₂O₃ sample, which should be attributed to the reduction of the octahedral Mo species and all Ni²⁺ species (Fig. 10c). Additionally, the reduction profile of the Mo species at 325-450 °C and 450-625 °C could be attributed to the reduction of the octahedral Mo species in well-dispersed polymolybdates and in different degrees of polymolybdates [53,67]. Meanwhile, a broad profile centered at 800 °C represents the deep reduction of all Mo⁴⁺ species and the reduction of isolated tetrahedral Mo species in strong interaction with the γ -Al₂O₃ support [67]. These results indicate that the Mo and Ni species on MZSM-5 are more easily reduced than those on γ -Al₂O₃.

To obtain information on metal sulfide active phases on the surfaces of MZSM-5 and γ -Al₂O₃, TEM was carried out. Generally, the NiMoS₂ active phases in metal sulfide catalysts can be subdivided into NiMoS₂-I (Type I) and NiMoS₂-II (Type II) [50,54,68]. The typical properties of the Type I phase are lower S coordination of Mo and Ni, and higher dispersion of the MoS₂, which are mostly single



Fig. 9. H_2 -TPR profiles of (a) Ni/MZSM-5, (b) Mo/MZSM-5, and (c) NiMo/MZSM-5 samples.



Fig. 10. H₂-TPR profiles of (a) Ni/ γ -Al₂O₃, (b) Mo/ γ -Al₂O₃, and (c) NiMo/ γ -Al₂O₃ samples.

slabs; and the Type II phase is fully sulfurized, has higher S coordination of Mo and Ni, and has less dispersion of the MoS₂, which are mostly multilayer slabs. In addition, the Type II phase has higher intrinsic activity than the Type I phase in the hydrogenation reaction [50,54,69]. Representative TEM images of the NiMoS/MZSM-5 and NiMoS/ γ -Al₂O₃ catalysts are shown in Fig. 11. It is clear that the less stacked MoS₂ crystallites with shorter length (black fringes) are highly dispersed on the surface of the γ -Al₂O₃, while the relatively multistacked MoS₂ crystallites with longer length are primarily located in the mesopore channels (Fig. 11a and insert) of the MZSM-5. The weak metal-MZSM-5 support interaction, discussed earlier, leads to the formation of MoS₂ crystallites with high stacking number and extended average length during sufidation [70]. The length and stacked layer number of the MoS₂ crystallites in the two sulfided catalysts was further statistically analyzed, and the results are shown in Fig. 12 and Table 3. The length and stacking of the MoS₂ slabs on the NiMoS/MZSM-5 catalyst are mainly 4–6 nm and 2–4 layers, respectively, greater than those on the NiMoS/ γ -Al₂O₃ catalyst (2–4 nm, 1–2 layers; Fig. 12). The average stacking and length of the MoS₂ slabs on the NiMoS/MZSM-5 are 3.3 and 5.9 nm, greater than those on NiMoS/ γ -Al₂O₃ (1.8 and 3.5 nm; Table 3). The MoS₂ slabs with more stacks and greater length would hamper the dispersion of the MoS₂ active phase [56]. Thus, the MoS₂ dispersion over NiMoS/γ-Al₂O₃ (0.29) is higher than over NiMoS/MZSM-5 (0.16; Table 3). Compared with NiMoS/MZSM-5, the higher MoS₂ dispersion on NiMoS/ γ -Al₂O₃ could be due to a change in the support properties. The silanol groups and acidic hydroxyl groups on MZSM-5 could interact weakly with the Mo species to benefit





Fig. 11. TEM images of (a) thin-sectioned NiMoS/MZSM-5 and (b) $NiMoS/\gamma\text{-}Al_2O_3$ catalysts.

the formation of polymolybdates and "free" MoO₃ species. They are easily transformed into multistacked MoS₂ active phases during sulifidation, resulting in lower f_{Mo} on NiMoS/MZSM-5 [54,56]. In contrast, the Mo species strongly interact with γ -Al₂O₃ via Mo—O—Al bridges, leading to the Mo species being difficult to sulfide into the MoS₂ active phase [50], and obtaining a high f_{Mo} on NiMoS/ γ -Al₂O₃. Therefore, the multistacked MoS₂ (Type II) active phases are more easily formed on the surface of the MZSM-5 relative to γ -Al₂O₃.

XPS experiments over sulfided catalysts were also performed to study the sulfidation degree of Mo and Ni species. The decomposition of the Mo3d spectra is shown in Fig. 13a. Molybdenum can exist as disulfide MoS_2 (Mo^{4+}) located at 229.0 ± 0.1 eV $(Mo^{4+}3d_{5/2})$ and 232.1 ± 0.1 eV $(Mo^{4+}3d_{3/2})$, as a Mo oxide phase (MoO_x, Mo^{6+}) located at 232.2 ± 0.1 eV $(Mo^{6+}3d_{5/2})$ and 235.3 ± 0.1 eV (Mo⁶⁺3 $d_{3/2}$), and as an intermediate state Mo oxysulfide (MoO_xS_v, Mo^{5+}) at 230.2 ± 0.1 eV $(Mo^{5+}3d_{5/2})$ and 233.4 ± 0.1 eV $(Mo^{5+}3d_{3/2})$ [71]. The higher atomic percentage of Mo⁴⁺ obtained for the NiMoS/MZSM-5 catalyst (Table 4) demonstrates that the sulfidation degree of the Mo species, defined as the ratio of Mo^{4+} to the sum of Mo^{4+} , Mo^{5+} , and Mo^{6+} [21], is higher on NiMoS/MZSM-5 than on NiMoS/ γ -Al₂O₃. In fact, the Mo⁴⁺ content depends inversely on the metal-support interaction [21]. The higher Mo4+ content of NiMoS/MZSM-5 could be attributed to the weaker molybdenum-support interaction [21], which favors the formation of octahedral Mo species on the MZSM-5, in agreement with the UV-vis and Raman results. The octahedral Mo species are easy to sulfide, leading to the formation of more MoS₂ active phases responsible for higher hydrogenation activity [54,56].

The Ni2p XPS spectra of the catalysts are shown in Fig. 13b. The binding energy of the Ni2p peaks at 856.1, 853.7, and 853.1 eV can

Fig. 12. Length (a) and layer stacking (b) distributions of MoS_2 slabs in NiMoS/MZSM-5 and NiMoS/ γ -Al₂O₃ catalysts.

be attributed to Ni^{2+} oxide species (including $NiAl_2O_4$ and NiO_x), NiMoS phase, and Ni sulfides (NiS_x) [71], respectively. The relative quantities of the Ni species (NiMoS, NiS_x, and Ni²⁺oxides) are shown in Table 4. The proportion of the NiMoS phase on the NiMoS/MZSM-5 catalyst (50.8%) is higher than that on the NiMoS/ γ -Al₂O₃ catalyst (25.6%), indicating that using mesoporous zeolites as a support increases the proportion of Ni-Mo interaction and leads to the formation of more NiMoS phases. Notably, the proportion of Mo⁴⁺ and NiMoS phase on the spent NiMoS/MZSM-5 catalyst is also higher than on the spent NiMoS/ γ -Al₂O₃ catalyst (Fig. S4 in the Supporting Information and Table 4). Nevertheless, the Ni content in the NiMoS phase on the NiMoS/MZSM-5 catalyst decreases after catalyst testing in phenanthrene hydrogenation. This is because the Ni species segregated from the MoS₂ edges and then aggregated into Ni²⁺ clusters. Such a phenomenon was also reported by Guichard and co-workers [72], and was explained in more detail by the dynamic model proposed by Nikulshin and colleagues [73,74]. In this model, the sulfur and promoters (Ni or Co) repeatedly migrated between the adjacent multilayered MoS₂ crystallites in the course of reduction-sulfidation processes under hydrogen, and the coke formed on the MoS₂ edge can block the promoters in the structure of neighboring layers. This led to the aggregation of promoter atoms. In our case, the TG analysis data show that the weight loss occurred on the spent NiMoS/MZSM-5 catalyst (Fig. S5 in the Supporting Information), which could be induced by coke formation. Coke formation could hinder the migration of the Ni atoms between the adjacent multilayered MoS₂ slabs and form separated Ni²⁺ clusters.

The atomic ratio of Mo/(Al + (Si)) in NiMoS/MZSM-5 is slightly lower than over NiMoS/ γ -Al₂O₃ (Table S1), indicating that relatively larger Mo species with lower dispersion are formed on MZSM-5. There is an obvious decrease in the Ni/(Ni + Mo) atomic ratio on the NiMoS/MZSM-5 catalyst due to more effective promotion of Ni species to MoS₂. Furthermore, the atomic ratio of S/Mo is much higher on NiMoS/MZSM-5 than on NiMoS/ γ -Al₂O₃, suggesting that the sulfidation degree of NiMoS/MZSM-5 is higher than



Fig. 13. Decomposition of XPS Mo3d (a) and Ni2p (b) spectra of NiMoS/MZSM-5 and NiMoS/ γ -Al₂O₃ catalysts.

Table 3

Average length and number of the stacking layers of MoS₂ crystallites.

Catalyst	Average length (nm)	Average stacking (number of layers)	f_{Mo}
NiMoS/MZSM-5	5.9	3.3	0.16
NiMoS/ γ -Al ₂ O ₃	3.5	1.8	0.29
NiMoS/MZSM-5-I	4.6	3.0	0.20
NiMoS/MZSM-5-L	3.7	2.4	0.22

Table 4

XPS results of the different contributions Mo3d and Ni2 $p_{3/2}$ obtained for sulfided catalysts.

Catalyst	Catalyst Mo distribution (at.%)		Ni distribution (at.%)			
	Mo ⁴⁺	Mo ⁵⁺	Mo ⁶⁺	NiMoS	NiS _x	Ni ²⁺
NiMoS/MZSM-5	81.1	10.5	8.5	50.8	24.4	24.8
NiMoS/ γ -Al ₂ O ₃	74.8	8.8	16.4	25.6	16.2	58.2
Spent NiMoS/MZSM-5	73.5	7.4	19.1	39.7	15.4	44.9
Spent NiMoS/γ-Al ₂ O ₃	68.9	9.0	22.1	25.1	20.1	54.7
NiMoS/MZSM-5-I	78.9	9.1	12.0	57.8	14.5	27.7
NiMoS/MZSM-5-L	78.5	11.5	10.0	66.2	9.3	24.5
NiMoS/ZSM-5	45.4	48.8	5.8	45.9	23.4	30.7

that of NiMoS/ γ -Al₂O₃. The higher sulfidation degree can be attributed to the relatively weak interaction between molybdenum species and MZSM-5 support.

3.2. Phenanthrene hydrogenation

Phenanthrene hydrogenation is a consecutive reaction that first creates dihydrophenanthrene (DHP) and 1,2,3,4-tetrahydrophenanthrene (THP), followed by the formation of symmetric and asymmetric octahydrophenanthrene (OHP) as well as perhydrophenanthrene (PHP) [75-77]. The reaction network of phenanthrene hydrogenation is shown in Fig. S6 in the Supporting Information. Fig. 14a shows the time dependence of phenanthrene conversion over various catalysts in the presence of 795 ppm sulfur in the form of dimethyldisulfide. Obviously, phenanthrene conversion over NiMoS/MZSM-5 catalyst is much higher than over NiMoS/ZSM-5, NiMoS/y-Al₂O₃, and Pd/MZSM-5 catalysts. Generally, the catalytic performance of supported metal sulfide catalysts is influenced by the support parameters, including the surface area, pore structure, and acidity. NiMoS/MZSM-5 has higher external surface area $(109 \text{ m}^2 \text{ g}^{-1})$ and mesopore volume $(0.14 \text{ cm}^3 \text{ g}^{-1})$, whereas NiMoS/ZSM-5 has lower external surface area $(40 \text{ m}^2 \text{ g}^{-1}, \text{ Table 1})$. Because the hydrogenation of the bulky phenanthrene molecule mainly occurs on the external surface and in the mesopores, the large mesopores in the NiMoS/MZSM-5 catalyst could favor mass transfer and result in higher phenanthrene conversion than on NiMoS/ZSM-5. In addition, the crystal MoS₂ phases could only form on the external surface (only 67 $m^2 g^{-1}$) of the ZSM-5, and not in the micropores $(0.54 \times 0.56 \text{ nm})$, due to the relatively large crystal dimension of



Fig. 14. Dependence of the (a) phenanthrene conversion and (b) DHPS selectivity on reaction time over (\blacksquare) NiMoS/MZSM-5, (\bullet) NiMoS/ γ -Al₂O₃, (\checkmark) Pd/MZSM-5, and (\diamond) NiMoS/ZSM-5 catalysts.

MoS₂ phases [54]. In contrast, MZSM-5 provides a large external surface area (175 m² g⁻¹), which could benefit the dispersion of the metal precursor and lead to the formation of more MoS₂ phases in the mesopore channels. This is supported by XPS analysis data (Table 4). The percentages of the Mo⁴⁺ species and NiMoS on the NiMoS/MZSM-5 (81.1% and 50.8%) are much higher than those on NiMoS/ZSM-5 (45.4% and 45.9%). These results indicate that more MoS₂ phases could be formed in the mesopores and provide more accessible active sites, further enhancing the catalytic activity of NiMoS/MZSM-5.

Although noble metal catalysts have higher hydrogenation activity than metal sulfide catalysts [2,4], the phenanthrene conversion over Pd/MZSM-5 is much lower than that over NiMoS/MZSM-5 under the same reaction conditions. This is because the Pd/MZSM-5 catalyst is easily poisoned by sulfur compounds, resulting in the deactivation of the catalyst [2,16]. As observed in the initial reaction stage, the phenanthrene conversion on Pd/MZSM-5 is rapidly reduced (Fig. 14a). In contrast, the NiMoS/MZSM-5 catalyst shows high initial activity and the conversion is not decreased with prolonged reaction time (Fig. 14a). Conventional NiMoS/ γ -Al₂O₃ catalyst has higher external surface area and mesopore volume (213 m² g⁻¹and 0.25 m³ g⁻¹) than NiMoS/MZSM-5 (109 m² g⁻¹ and 0.14 m³ g⁻¹), but it is still difficult to obtain higher phenanthrene conversion. For example, the conversion over NiMoS/ γ -Al₂O₃ (80.5%) catalyst is much lower than that over NiMoS/MZSM-5 (98.7%) catalyst at a reaction time of 40 h (Table 5). To further compare the capability of deep hydrogenation of phenanthrene over various catalysts, the dependence of the sum of OHP and PHP (products of deep hydrogenation of phenanthrene, DHPS) with reaction time is shown in Fig. 14b. Very interestingly, the DHPS selectivity over NiMoS/MZSM-5 is much higher than over NiMoS/ γ -Al₂O₃. For instance, the DHPS selectivity over NiMoS/MZSM-5 is 98.6%, and those over NiMoS/ γ -Al₂O₃ and Pd/MZSM-5 are 51.6% and 3.2% (Table 5), respectively. These results indicate that the mesoporous zeolites are better supports for preparing metal sulfide catalysts with high hydrogenation activity. In addition, compared with NiMoS/MZSM-5 catalyst, the activity of NiMoS/ γ -Al₂O₃ decreased rapidly in the initial stage. In general, the deactivation of the metal sulfide catalyst is mainly induced by coke formation and the reduction of the active phases [72]. In the present work, the TG analysis shows that the weight loss of the spent NiMoS/ γ -Al₂O₃ catalyst is significant compared with that of the spent NiMoS/MZSM-5 catalyst (Fig. S5 in the Supporting Information). The coke hydrocarbons might adsorb onto the active sites and lead to deactivation of the catalysts [72].

In the absence of mass and heat transfer effects, the observed reaction rate (r_{obs}) and TOF of phenanthrene hydrogenation over catalysts are presented in Table 6. The r_{obs} and TOF for NiMoS/MZSM-5 ($7.4 \times 10^{-4} \text{ mol kg}^{-1} \text{ s}^{-1}$ and $15.0 \times 10^{-4} \text{ s}^{-1}$) catalyst are much higher than for NiMoS/ γ -Al₂O₃ catalyst ($4.8 \times 10^{-4} \text{ mol kg}^{-1} \text{ s}^{-1}$ and $8.9 \times 10^{-4} \text{ s}^{-1}$). In addition, the selectivity of the deep hydrogenation product (OHP) over NiMoS/MZSM-5 is much higher than that over NiMoS/ γ -Al₂O₃ (Table 6). These results suggest that the NiMoS/MZSM-5 catalyst

Table 5

Product selectivity in phenanthrene hydrogenation over various catalysts at reaction time of 40 h.

Run	Catalyst	PHE conv. (%)	Product selectivity (%)				
			DHP	THP	OHP	PHP	DHPS ^a
1	NiMoS/MZSM-5	98.7	-	1.4	80.7	17.9	98.6
2	NiMoS/γ-Al ₂ O ₃	80.5	34.6	13.8	51.6	-	51.6
3	NiMoS/ZSM-5	21.2	51.4	40.5	8.1	-	8.1
4	Pd/MZSM-5	38.3	77.8	19.0	3.2	-	3.2

^a The sum of OHP and PHP (deep hydrogenation products, DHPS).

has a hydrogenation capability superior to that of the conventional NiMoS/ γ -Al₂O₃ catalyst. The higher activity of the NiMoS/MZSM-5 catalyst could be assigned to the difference in surface properties of the γ -Al₂O₃ and MZSM-5 supports. Acidic hydroxyl and silica hydroxyl groups existed on the MZSM-5, which interacted weakly with the Mo species to benefit the formation of polymolybdates and "free" MoO₃ species on the MZSM-5 during the catalyst pretreatment process. After sulfidation, the polymolybdates and "free" MoO₃ species can easily be transformed into more multistacked MoS₂ active phases that favor the adsorption of aromatics and therefore enhance the hydrogenation activity of the catalyst [69]. In contrast, basic hydroxyl groups existed on the γ -Al₂O₃, which interacted strongly with the Mo species, facilitating the formation of isolated MoO_4^{2-} species that are difficult to sulfide into the MoS_2 active phases [50,58]. The details were discussed in the characterizations.

It is important that the NiMoS/MZSM-5 catalyst shows a long catalyst life (Fig. S7 in the Supporting Information). There is no activity loss in phenanthrene hydrogenation. The good catalyst life of the NiMoS/MZSM-5 catalyst is one of the key factors for practical application in industry. It is worth mentioning that the NiMoS/MZSM-5 catalyst has relatively low acidity, slightly lower than that of the NiMoS/ γ -Al₂O₃ catalyst (Fig. 6 and Table 2). Thus, compared with NiMoS/ γ -Al₂O₃ catalyst, the higher activity of the NiMoS/MZSM-5 catalyst is not caused by the acidity. Not only the NiMoS/MZSM-5 but also the CoMoS/MZSM-5 catalyst has excellent deep hydrogenation activity in phenanthrene hydrogenation (Fig. S8 in the Supporting Information). The phenanthrene conversion and DHPS selectivity over CoMoS/MZSM-5 catalyst (88.1% and 95.4%) are higher than those over CoMoS/ γ -Al₂O₃ (80.8% and 47.0%) catalyst (Table S2). In addition, the mesostructured mordenite-supported NiMo and CoMo catalysts also show high conversion and deep hydrogenation ability in phenanthrene hydrogenation in comparison with γ -Al₂O₃ supported ones (Fig. S8).

3.3. Relationship between morphology of active phase and catalytic performance

Generally, the stacking and slab length of the MoS₂ crystallites strongly influence the intrinsic activity of the catalyst [56,65,78]. Because the stacking and slab length of the MoS₂ crystallites could be controlled by varying the Mo loadings on the support, it is possible to establish the relationship between the slab length and stacking of the MoS₂ and hydrogenation activity by using different Mo loading catalysts. Fig. S9 in the Supporting Information shows representative TEM images of MZSM-5-supported NiMo catalysts with different metal loadings (3.0, 6.0, and 12.0 wt.% Mo). Fig. S10 in the Supporting Information shows the distribution of the lengths and stacking of MoS₂ slabs on the catalysts. The length and stacking of the MoS₂ slabs clearly increase with Mo loading (Figs. S9 and S10). The average length and stacking of the MoS₂ slabs also increase with Mo loading (Table 3).

From Tables 3 and 6, it is clear that the TOF value increases with a decrease in the average length and average stacking of the MoS₂ phase on the MZSM-5 support. This result suggests that the intrinsic activities of the metal sulfide catalysts could correlate with the morphology (length and stacking number) of MoS₂ crystallites. Nikulshin and co-workers also reported that the hydrogenation activity of the NiW and Co(Ni)Mo catalysts supported on γ -Al₂O₃ increased with the decrease in slab length and Ni/W(Mo)_{edge} ratio of the active phase [65,78]. In addition, the MoS₂ particles with shorter slab length and relatively less stacking could provide more exposure of the edge of MoS₂ slabs, leading to an increase in the available sites for Ni promotion [65]. Therefore, compared with NiMoS/MZSM-5-I catalysts, the NiMoS/MZSM-5-L catalyst presents the highest dispersion of MoS₂ particles with short slab length

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Tabla	~

Phenanthrene	hydrogenation	performance	over	various	catalysts.

Catalyst	$r_{obs} imes 10^4 \ (m mol \ kg^{-1} \ s^{-1})$	$r'_{obs} imes 10^4 \; (m mol \; kg^{-1} \; s^{-1})^a$	$\textit{TOF} \times 10^4~(s^{-1})^b$	$\mathit{TOF}_{\mathit{Mo}^{4+}} imes 10^4 \ (s^{-1})^{\ c}$	Produc	Product selectivity ^d (%)		
					DHP	THP	OHP	PHP
NiMoS/MZSM-5	7.4	6.7	15.0	18.0	31.3	47.7	20.9	-
NiMoS/ γ -Al ₂ O ₃	4.8	4.3	8.9	12.0	38.7	46.1	15.2	-
NiMoS/MZSM-5-I	-	7.1	18	_	31.9	48	20.1	-
NiMoS/MZSM-5-L	-	7.7	20	-	34.5	47	18.5	-

^a The observed reaction rate calculated per Mo atom in the sulfide catalyst, $r'_{obs} = \frac{dx}{d(N_{two}/F)}$

^b The number of reacted PHE molecules per second and per Mo atom at the edge surface. ^c TOF transformed per mol of Mo⁴⁺ sites determined from XPS, $TOF_{M0^{4+}} = \frac{F \times X}{N_{M0^{4+}} \times f_{M0^{4-}}}$.

^d Determined at about 20% of total phenanthrene conversion by changing the weight hourly space velocity.

and less stacking, which favors the formation of more Ni-promoted MoS₂ active sites and NiMoS₂ Type II phases. XPS analysis also shows that the Ni content in the NiMoS phase is 66.2, 57.8, and 50.8% in the NiMoS/MZSM-5-L, NiMoS/MZSM-5-I, and NiMoS/MZSM-5 catalysts (Table 4). Based on these results, it can be concluded that the catalytic activity depends on the number of NiMoS phases as well as the shape of the active phase crystallites. In addition, although the highest TOF number is obtained over the NiMoS/MZSM-5-L catalyst with the lowest metal loading, an optimal balance could be achieved between the catalytic activity and catalyst loading in the feedstock.

4. Conclusions

Mesoporous ZSM-5 was successfully synthesized using a waterglass-containing cationic copolymer with quaternary ammonium groups as a template, and applied for preparation of highly active metal sulfide catalysts. Compared with γ -Al₂O₃-supported NiMo (or CoMo) catalysts, the MZSM-5-supported NiMo (or CoMo) catalysts show very high activity in the deep hydrogenation of phenanthrene. This feature is attributed to the fact that more multistacked MoS₂ active phases are formed on the MZSM-5 due to the weaker metal-support interaction relative to γ -Al₂O₃. In addition, the catalytic activity depends on the number of NiMoS phases as well as the shape of the active phase crystallites.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2015.07.026.

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