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Effects of preparation conditions in hydrothermal synthesis of highly active unsupported NiMo sulfide catalysts for simultaneous hydrodesulfurization of dibenzothiophene and 4,6-dimethyldibenzothiophene

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ABSTRACT

Unsupported NiMo sulfide catalysts were prepared from ammonium tetrathiomolybdate (ATTM) and nickel nitrate by using a hydrothermal synthesis method involving water, organic solvent and hydrogen. The activity of these catalysts in the simultaneous hydrodesulfurization (HDS) of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) was much higher than that of the commercial $NiMo/Al_2O_3$ sulfide catalysts. Interestingly, the unsupported NiMo sulfide catalysts showed higher activity for hydrogenation (HYD) pathway than the direct desulfurization (DDS) pathway in the HDS of DBT. The same trends were observed for the HDS of 4,6-DMDBT. Morphology, surface area, pore volume and the HDS activity of unsupported NiMo sulfide catalyst depended on the catalyst preparation conditions. Higher temperature and higher H_2 pressure and addition of an organic solvent were found to increase the HDS activity of unsupported NiMo sulfide catalysts for both DBT and 4,6-DMDBT HDS. Higher preparation temperature increased HYD selectivity but decreased DDS selectivity. High-resolution TEM images revealed that unsupported NiMo sulfide prepared at 375 °C shows lower number of layers in the stacks of catalyst with more curvature and shorter length of slabs compared to that prepared at 300 °C. On the other hand, higher preparation pressure increased DDS selectivity but decreased HYD selectivity for HDS of 4,6-DMDBT. HRTEM images showed higher number of layers in the stack for the NiMo sulfide prepared under an initial H_2 pressure of 3.4 MPa compared to that under 2.1 MPa. The optimal Ni/(Mo + Ni) ratio for the NiMo sulfide catalyst was 0.5, higher than that for the conventional Al_2O_3-supported NiMo sulfide catalysts. This was attributed to the high dispersion of the active species and more active NiMoS generated. The present study also provides new insight for controlling the catalyst selectivity as well as activity by tailoring the hydrothermal preparation conditions.

1. Introduction

The challenge of fulfilling the world's growing transportation energy needs is no longer a simple issue of producing enough liquid hydrocarbon fuels. This challenge is accentuated by a complex interplay of environmental and operational issues. Environmental issues include societal demands that liquid hydrocarbon fuels are clean and least polluting. The emergence of new refining processes and the increasing use of new forms of energy production, e.g. fuel cells, exemplify operational issues. Together, these trends are driving the need for deep desulfurization catalysts. Such a demand for more active hydrodesulfurization (HDS) catalysts has triggered a significant increase in research activity on HDS catalyst development [1–3]. These studies have shown that one way to improve the performance of MoS_2-based catalysts could be to increase the active phase loading or use bulk sulfides. The emergence of highly loaded sulfide catalysts demonstrates that sulfide-based systems still have great potential for improvement.

Conventional catalysts used in the hydrotreating process include mainly Ni or Co promoted Mo- or W-based catalysts supported by γ-Al_2O_3 [4]. They are active in converting thiophene

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and benzothiophenes, but not active enough to desulfurize efficiently the most refractory sulfur-containing polyaromatic compounds, e.g. dibenzothiophene (DBT) and its alkyl-substituted derivatives which are the major portion of sulfur in the high-boiling fraction of crude oil and middle distillates of refinery streams such as light cycle oil. In 1997, Gates and Topsoe [5] pointed out that 4-MDBT (4-methyldibenzothiophene) and 4,6-DMDBT are the most appropriate compounds for investigation of candidate catalysts and reaction mechanism.

It is well established that Mo-based catalysts used for HDS reactions are promoted by the addition of cobalt or nickel in much more than trace amounts. The synergetic effects of promoter on the catalytic activity of the Mo sulfides have been reported by many researchers in the literatures [6–8]. The effect of promoter in Mo sulfide catalysts on HDS reactions has been attributed to the amount of promoter atoms that can be accommodated on the edges of MoS_2 layers and also to the electronic transfer that the promoter atom induces on Mo atoms located at these sites [9,10].

Generally, Mo sulfide catalysts are prepared by an impregnation of aqueous solution of oxide precursors on Al_2O_3 support, followed by drying, calcination and presulfidation with either H_2/H_2S or an organic sulfur compound such as dimethyldisulfide (DMDS) [11]. An alternative to prepare sulfide catalysts is to use precursor compounds already sulfided-like alkyl ammonium thiometalates precursors $(NR_4)_2MeS_4$ (R: alkyl or H; Me: Mo or W). Some researchers have proposed effective preparation of Mo sulfide catalysts with precursors such as ammonium tetrathiomolybdate (ATTM) [7,8,12–15]. These Mo sulfide catalysts can be synthesized directly via a thermal decomposition of ATTM and do not need further presulfidation. Devers et al. [16] observed the relatively high activity of Mo sulfide catalysts prepared via hydrothermal method compared with the Mo sulfide catalysts prepared by thermal decomposition. Recently, Song et al. [17,18] reported a new method for preparing the highly dispersed unsupported Mo sulfide catalyst from aqueous ATTM solution mixed with an organic solvent via hydrothermal synthesis under hydrogen. The use of organic solvent helps to improve the dispersion of the precursor molecules. While unsupported Mo sulfide catalysts have been often used as model catalysts for hydrotreating reactions, their high activities could become more attractive for commercial applications.

Our previous work [19] showed that hydrothermal synthesis using water and organic solvent under hydrogen could produce highly active Mo-based sulfide nano-size particles. Promoter (Ni and Co) affects both the number and the activity of active site of Mo sulfides. Temperature programmed reduction showed the close interaction between Ni or Co and Mo in the bimetallic sulfide catalysts resulting in shift of TPR peaks to lower temperatures upon Ni or Co addition to MoS_2. In the present study, unsupported NiMo sulfide catalysts were prepared using ATTM by hydrothermal method. This paper focuses on the effects of preparation conditions on the activity and selectivity of unsupported NiMo sulfide catalysts for the simultaneous hydrodesulfurization of DBT and 4,6-DMDBT.

2. Experimental

2.1. Materials

Ammonium tetrathiomolybdate ($(NH_4)_2MoS_4$), nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT) and decahydronaphthalene (decalin, used as solvent) were purchased from Aldrich Chemical Company and were used without further purification. It was noted that the long-time storage of ATTM in closed vials that was exposed to air may lead to degradation of the reagent resulting in deviations in the observed activity of in-situ generated MoS_2 catalysts from different bottles of ATTM reagent. In this work, a bottle of newly purchased ATTM was used in synthesis, and the ATTM reagent was stored in a refrigerator in order to minimize oxidative degradation.

2.2. Catalyst synthesis and characterization

Unsupported NiMo sulfide catalysts were synthesized by using the hydrothermal method involving water, an organic (hydrocarbon) solvent and hydrogen. The catalyst synthesis was carried out in a 25 mL batch reactor. Typically, ATTM and $Ni(NO_3)_2{\cdot}6H_2O$ were dissolved in 10 g of de-ionized water. The atomic ratio of Ni/(Mo + Ni) was varied in the range of 0–0.56. Then, an organic solvent decalin was added. The reactor was sealed and purged with hydrogen before being pressurized to a desired initial pressure and placed in a preheated fluidized sand bath for 2 h under vertical agitation. Subsequently, the reactor was removed from the sand bath and immediately quenched in water bath. The unsupported catalysts synthesized were separated and immerged under an organic solvent before use.

The commercial-supported catalyst $NiMo/Al_2O_3$ (Cr424) obtained from the Criterion Catalyst Company was used to compare the activity with the synthesized unsupported Mo-based sulfide catalysts for the HDS of 4,6-DMDBT and DBT. The catalyst was crushed to a particle size of <1 mm and presulfided at 350 °C for 4 h in a flow of 5 vol.% H_2S/H_2 at flow rate of 150 ml/min. The sulfided catalyst was subsequently stored in decalin to minimize oxidation. The specific surface area is 163 m^2/g.

The N_2 adsorption and desorption isotherms were measured on a Micromeritics ASAP 2020 instrument. Pore size distributions of the samples were determined from the isotherms by the Barrett–Joyner–Hallenda (BJH) method. Fresh catalyst samples were vacuum-dried before the adsorption measurement. The X-ray diffraction (XRD) patterns were obtained on a Scintag Powder Diffractometer with Cu Kα emission, 30 mA 35 kV with a scanning speed of 2°/min. The diffractograms were analyzed using the standard JCPDS files. The high-resolution transmission electron microscopy (HRTEM) was performed on a JEOL JEM-2010F transmission electron microscope. A small amount of sample was ground with a mortar and pestle. The sample was then suspended in ethanol and sonicated. A drop of the suspension was put on a lacey carbon film supported by a Cu grid.

2.3. Hydrodesulfurization reaction

Catalytic activity and selectivity of metal sulfides were evaluated with a simultaneous HDS of DBT and 4,6-DMDBT in a 25 mL horizontal tubing micro-reactor. The reactor was loaded with 0.023 g synthesized catalyst and 4 g reactant mixture (0.4% mole 4,6-DMDBT and 0.4% mole DBT in decalin). The sealed reactor was purged with hydrogen then pressurized up to 2.8 MPa and placed in a fluidized sand bath which was preheated up to 350 °C for 30 min. The reactor was vertically agitated at a rate of 200 strokes/min; the reaction was not diffusion controlled. After the reaction, the reactor was removed from the sand bath and immediately quenched in a cold-water bath. Finally, liquid products and the catalysts were collected. The liquid products were identified by GC/MS (Shimadzu GC12A/QP-500) and quantitatively analyzed with a GC-FID (HP5890) with a XTI-5 column (Restek). Both GC/MS and GC-FID were programmed from 55 to 240 °C at heating rate of 5 °C/min. The DBTs conversion is defined as {100 × [initial DBTs − final DBTs]/initial DBTs}. Duplicate or triplicate experiments were performed and the average of duplicated tests is reported here. The errors for conversion values were typically within plus/minus 1.5 wt.%. The HYD/DDS ratio is defined as [selectivity to (THDBT + CHB + BCH)/selectivity to BP].

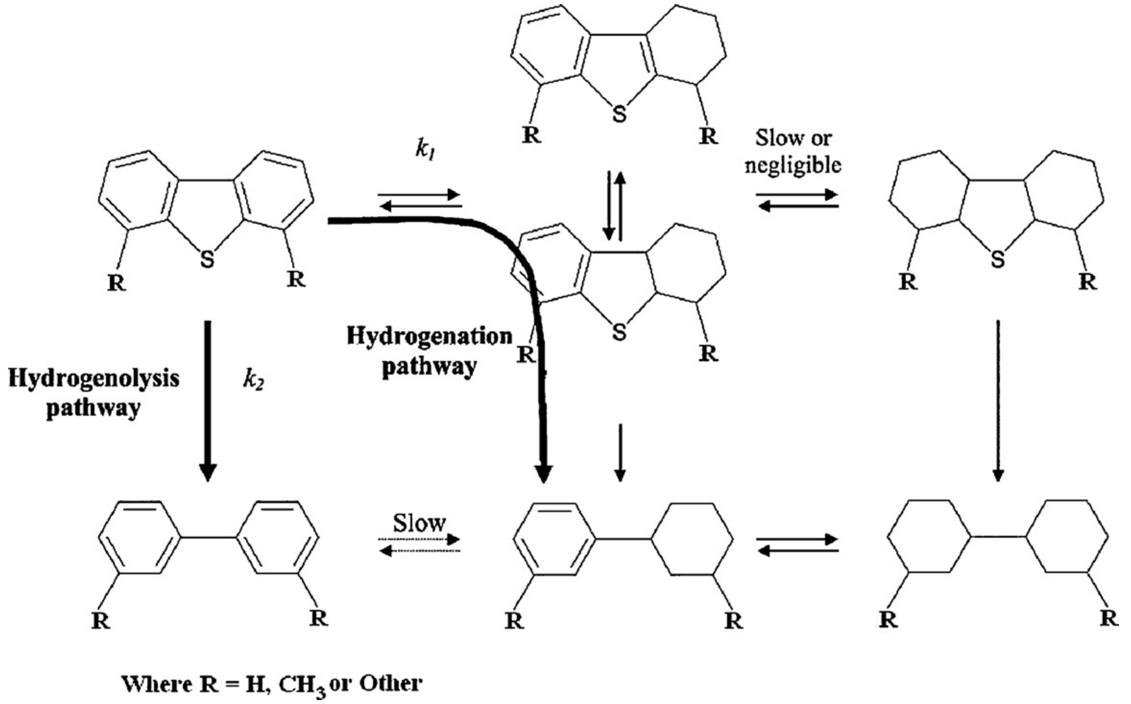

Fig. 1. Reaction pathways of desulfurization of polyaromatic sulfur compounds via a ring hydrogenation network (denoted by the rate constant k_1) and a direct C–S bond hydrogenolysis network (denoted by the rate constant k_2) (adapted from [45]).

3. Results and discussion

Hydrodesulfurization of DBT-type sulfur compounds generally proceeds through two pathways as shown in Fig. 1. The direct-desulfurization (DDS) or hydrogenolysis path involves chemisorption of the sulfur atom in the reactant molecule on an exposed Mo ion at a sulfur vacancy, which is followed by hydrogen transfer and sulfur elimination to complete desulfurization [20]. The HDS of DBT occurs predominantly via the DDS pathway. However, hydrogenolysis does not saturate the benzene rings in 4,6-DMDBT. Therefore, HDS catalysts promoting the hydrogen-efficient hydrogenolysis route to HDS are generally considered to be more desirable. The second path is called hydrogenation (HYD) involving the adsorption of sulfur compounds on the MoS_2 stack through the π-electrons on the aromatic rings. This is followed by hydrogenation of one of the aromatic rings and then carbon–sulfur bond cleavage to complete desulfurization. 4,6-DMDBT is generally desulfurized through the HYD pathway because the direct adsorption of 4,6-DMDBT on the active sites is hindered by the two-methyl groups at the 4- and 6-positions. If 4,6-DMDBT is hydrogenated to tetrahydro- or hexahydro-DMDBT, this steric hindrance is reduced and the electron density on the S atom is increased, rendering the hydrogenated 4,6-DMDBT desulfurized more easily [21–23].

3.1. Effect of catalyst preparation conditions on HDS activity of NiMo sulfide catalysts

3.1.1. Catalyst preparation temperature

Fig. 2 shows the effects of catalyst preparation temperature on the activity of unsupported NiMo sulfide catalysts for the DBT and 4,6-DMDBT HDS. When the preparation temperature was increased from 300 to 375 °C, the conversion of DBT and 4,6-DMDBT increased gradually from 50.3% to 63.9% and from 41.6% to 51.9%, respectively. The DBT conversion was approximately 1.2 times the 4,6-DMDBT conversion. Table 1 presents the product distribution in the DBT and 4,6-DMDBT HDS over NiMo sulfide catalysts prepared at various temperatures. The selectivity to biphenyl (BP) and cyclohexylbenzene (CHB) which were the major products of DBT HDS showed different trends. The CHB selectivity (from HYD pathway) increased while the BP selectivity (from DDS pathway) decreased when the catalyst preparation temperature was increased. However, the selectivity of tetrahydrodibenzothiophene (THDBT) and bicyclohexane (BCH), the minor products, did not change significantly.

The product selectivity of 4,6-DMDBT HDS is different from that in DBT HDS. Tetra-hydrodimethyldibenzothiophene (THDMDBT) was the major product from hydrogenation along with methylcyclohexyltoluene (MCHT) from HYD path, together with 3,3′-dimethylbiphenyl (3,3′-DMBP). Similar to the DBT HDS product distribution, 3,3′-DMBP, a product from DDS pathway, decreased when catalyst preparation temperature was increased, while the products from the HYD pathway (THDMDBT and MCHT) increased.

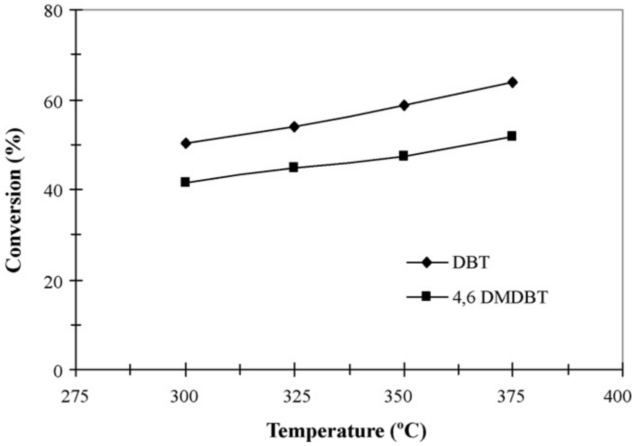

Fig. 2. Effect of preparation temperature on simultaneous HDS of DBT and 4,6-DMDBT over unsupported NiMo sulfide catalysts (other preparation parameters: pressure = 2.8 MPa, solvent amount = 1 g, Ni/(Mo + Ni) = 0.43).

Table 1

Effect of preparation temperatures and pressures in catalyst preparation on simultaneous HDS of 4,6-DMDBT and DBT over unsupported NiMo sulfide catalysts at 2.8 MPa and 350 °C for 30 min (other catalyst preparation parameters: solvent amount = 1 g and Ni/(Mo + Ni) = 0.43).

Preparation temperature (°C)	300	325	350	375	350	350	350
Preparation H_2 init. pressure (MPa)	2.8	2.8	2.8	2.8	1.4	2.1	3.4
DBT conversion (wt.%)	50.3	53.8	58.5	63.9	39.8	54.2	63.4
Selectivity (%)							
THDBT	5.2	5.4	6.2	4.9	10.9	9.5	5.6
BP	46.5	43.4	41.1	38.7	51.4	37.4	45.0
CHB	39.6	42.0	42.6	47.1	31.6	43.1	40.8
BCH	8.7	9.2	10.1	9.3	6.1	10.0	8.6
HYD/DDS[a]	1.2	1.3	1.4	1.6	0.9	1.7	1.2
4,6-DMDBT conversion (wt.%)	41.6	44.8	47.3	51.9	29.4	40.4	50.5
Selectivity (%)							
THDMDBT	33.7	35.6	37.8	41.8	45.6	41.9	35.3
3,3′-DMBP	40.6	37.1	33.2	25.4	29.4	31.4	32.8
MCHT	24.0	25.8	27.0	31.0	21.7	24.5	28.9
DMBCH	1.7	1.5	2.0	1.8	3.3	2.2	3.0
HYD/DDS[b]	1.5	1.7	2.0	2.9	2.4	2.2	2.0
DBT/4,6-DMDBT conv ratio	1.2	1.2	1.2	1.2	1.4	1.3	1.3

[a] HYD/DDS = [selectivity to (THDBT + CHB + BCH)/selectivity to BP].

[b] HYD/DDS = [selectivity to (THDMDBT + MCHT + DMBCH)/selectivity to 3,3′-DMBP].

The selectivity to 3,3′-DMBCH, the minor product, did not change significantly. Consequently, the HYD/DDS ratio increased from 1.2 to 1.6 for the DBT HDS and from 1.5 to 2.9 for the 4,6-DMDBT HDS with increasing preparation temperature from 300 to 375 °C.

The specific surface areas of the unsupported NiMo sulfide catalysts prepared at various temperatures are shown in Table 2. In general, increasing the preparation temperature increased both the surface area and pore volume of the resulting catalysts which are largely mesoporous. The highest surface area (249 m^2/g) and pore volume (0.39 cm^3/g) were observed when catalyst was prepared at temperature of 375 °C while the catalyst with lower surface area (121 m^2/g) and pore volume (0.19 cm^3/g) was obtained when a lower preparation temperature (300 °C) was used.

Fig. 3 presents the HRTEM images of unsupported NiMo sulfide catalysts prepared at 300 and 375 °C, respectively. The black thread-like fringes in Fig. 3 correspond to the MoS_2 slabs. The fringes observed in the images had a spacing of about 0.65 nm that was the characteristic of (0 0 2) basal planes of crystalline MoS_2. The HRTEM images clearly showed that the average number of layers in the stacks of catalyst prepared at 300 °C was higher (6–10 layers, Fig. 3A) than that of the catalyst prepared at 375 °C (2–4 layers, Fig. 3B). Furthermore, the catalyst prepared at lower temperature had long slabs. The curvature of slabs increased while the slab length decreased upon the increasing in the preparation temperature.

The above results can be better rationalized by considering that the catalytic activity and selectivity of Mo-based sulfide catalyst depends on the coexistence of two different sites that promote HDS through the DDS pathway and the HYD pathway. A very useful "Rim-Edge" model for MoS_2 stacks (slabs) has been proposed in 1994 by Daage and Chianelli [24]. In this model, the MoS_2 catalyst is described as stacks of several discs; the top and bottom discs are associated with rim sites (HYD sites) that catalyze predominantly hydrogenation of large molecules such as DBT; the discs "sandwitched" between the top and bottom discs are associated with edge sites and sulfur removal from large molecules is catalyzed mainly by edge sites (DDS). How the rim sites catalyze hydrogenation of DBT and DMDBT was not clear from the Rim-Edge model. In another earlier study, Tanaka reported that by cutting perpendicularly to basal plane of MoS_2 single crystal into several pieces the catalytic selectivity of the reaction could be modified [25]. This single crystal cutting increased the area of the edge planes while the area of the basal planes stayed constant. This cutting increases hydrogenation activity of catalyst. More recent studies by Topsoe, Besenbacher, Nørskov and their coworkers using advanced in-situ spectroscopic techniques coupled with experimental and computational correlations have revealed that there exist metallic-like brim sites which are located adjacent to the edge of Mo sulfide slabs and such brim sites are active for hydrogenation [26–28]. The brim sites location is different from that in the previously proposed rim sites or corner sites. It is important to note that only the top layer of multi-stacks of CoMo and NiMo sulfides will expose the brim sites which play a key role for hydrogenation reactions [26]. These new findings allow us to better understand the importance of the slab length and slab stacking layers of Mo sulfide catalysts.

Table 2

Surface area and pore volume of fresh NiMo sulfide catalysts prepared at various preparation temperatures and pressures (other catalyst preparation parameters: solvent amount = 1 g and Ni/(Mo + Ni) = 0.43).

Preparation temperature (°C)	Preparation pressure (MPa)	Surface area (m^2/g)	Pore volume (cm^3/g)
300	2.8	121	0.19
325	2.8	158	0.21
350	2.8	201	0.28
375	2.8	249	0.39
350	1.4	83	0.17
350	2.1	161	0.22
350	3.4	231	0.37

According to the above-mentioned advances in structure-activity correlations, catalysts with a predominance of single unstacked layers will have a greater selectivity to hydrogenated products than those with a predominance of stacked layers. In the same context, catalysts with lower number of layers in stacks and/or with shorter slabs will have higher hydrogenation activity than the catalysts with higher number of layers in stacks and or with longer slabs.

From the present HDS and HRTEM results on the effect of preparation temperature, it appears that there are relatively more HYD sites than the DDS sites on the unsupported NiMo sulfide

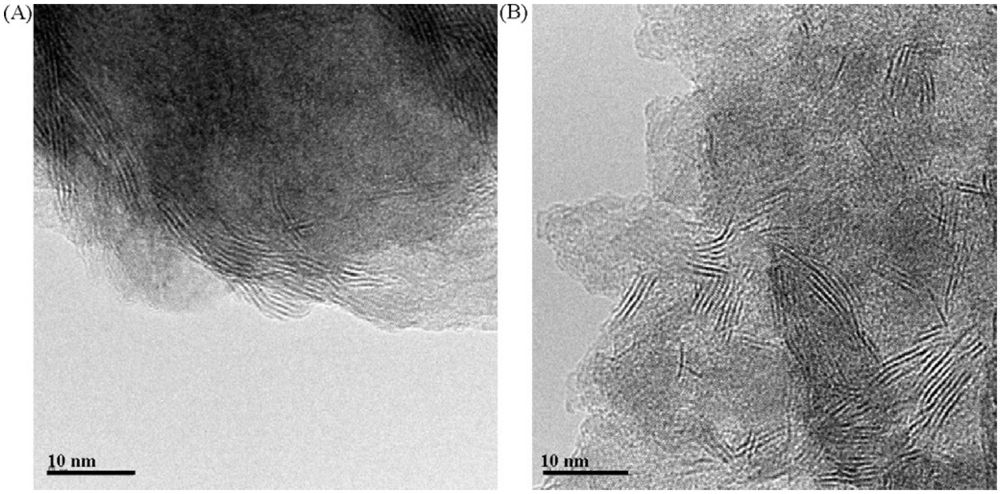

Fig. 3. High-resolution TEM images of unsupported NiMo sulfide catalysts prepared at difference temperatures: (A) 300 °C; (B) 375 °C.

catalysts prepared at higher temperature. The catalyst prepared at lower temperature had higher number of layers and long slabs and it showed lower hydrogenation selectivity. On the other hand, the catalyst prepared at higher temperature had lower number of layers and short slabs and it showed higher hydrogenation selectivity. The HRTEM images are consistent with the observed results on the ratio of HYD/DDS in the product selectivity.

Based on the above results and discussion, it is highly likely that the NiMo sulfide catalysts prepared at higher temperatures under the hydrothermal conditions in this work possess larger numbers of the brim sites (adjacent to the edge on the top layer of Mo-based sulfides) that have been recently discovered and shown to be active for hydrogenation by Topsoe, Besenbacher, Nørskov and their coworkers [26–28].

3.1.2. Catalyst preparation pressure

Fig. 4 shows the effect of catalyst preparation pressure on the subsequent hydrodesulfurization. Similarly to the catalyst preparation temperature effect, a gradual increase in the conversion of 4,6-DMDBT and DBT was observed when H_2 pressure in catalyst preparation was increased. In the pressure range of 1.4–3.4 MPa, H_2 pressure in catalyst preparation showed a remarkably strong effect on the HDS activity of resulting catalyst. The DBT and 4,6-DMDBT conversion increased from 39.8% to 63.4% and from 29.4% to 50.5%, respectively.

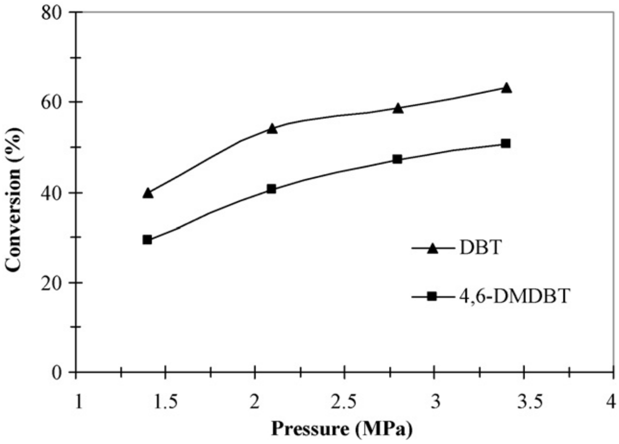

Fig. 4. Effect of preparation pressure of H_2 on simultaneous HDS of DBT and 4,6-DMDBT over unsupported NiMo sulfide catalysts (other preparation parameters: temperature = 350 °C, solvent amount = 1 g, Ni/(Mo + Ni) = 0.43).

Product distributions for the DBT and 4,6-DMDBT HDS are presented in Table 1. For the DBT HDS, generally, BP was a major product from the DDS pathway. However, it is very interesting to note that the major product from HYD pathway was CHB. The THDBT and BCH amount was detected around 6–10%. The HYD/DDS ratio was over 1.0 for all catalysts except for the NiMo sulfide prepared at 1.4 MPa, which had the HYD/DDS ratio of 0.9. In the pressure range of 1.4–2.1 MPa, the selectivity to CHB increased from 31.6% to 43.1% while the selectivity to BP decreased from 51.4% to 37.4%. Increasing pressure further to 3.4 MPa, the reverse trends were observed. The results showed that there are mixed effects of preparation pressure on hydrogenation and direct desulfurization pathway of DBT HDS. Initially, it favors hydrogenation pathway, but above 2.1 MPa the direct removal of sulfur is more favorable.

For the 4,6-DMDBT HDS, THDMDBT, 3,3′-DMBP and MCHT were the major products while DMBCH amount were detected around 2.0% to 3.3%. Unlike the preparation temperature effect, the 3,3′-DMBP selectivity from DDS pathway did not show a considerable change but the selectivity to THDMDBT from HYD pathway decreased significantly from 45.6% to 35.3% when the catalyst preparation pressure was increased from 1.4 to 3.4 MPa. The HYD/DDS ratio of 4,6-DMDBT HDS also decreased from 2.4 to 2.0 when the preparation pressure was increased. The results showed that unsupported NiMo sulfide catalysts prepared at higher H_2 pressure became less selective for HYD pathway, but more selective for DDS pathway for HDS of 4,6-DMDBT.

These results indicate that the H_2 pressure for catalyst preparation significantly affects the HDS activity of the resulting NiMo sulfide catalysts. In the decomposition of ATTM, hydrogen is necessary for forming the catalytically active bimetallic sulfide. More detail on formation of the bimetallic sulfide in the presence of hydrogen is described in the Section 3.3.2. The higher H_2 pressure increased the activity of NiMo sulfide catalysts for both DBT and 4,6-DMDBT HDS. The low H_2 pressure might not provide enough hydrogen for the decomposition and the reaction of ATTM. Possibly, the higher H_2 pressure assisted the reaction and conversion of ATTM and Ni precursor to NiMo sulfide with a more porous and more active phase for DBT and 4,6-DMDBT HDS.

The specific surface area and pore volume of catalysts prepared at difference H_2 pressure are shown in Table 2. Similar to the preparation temperature effect, higher preparation pressure leads to higher surface area and larger pore volume. The unsupported NiMo sulfide catalyst prepared at an initial H_2 pressure of 1.4 MPa has a lower surface area of 83 m^2/g, that prepared at 2.1 MPa has a

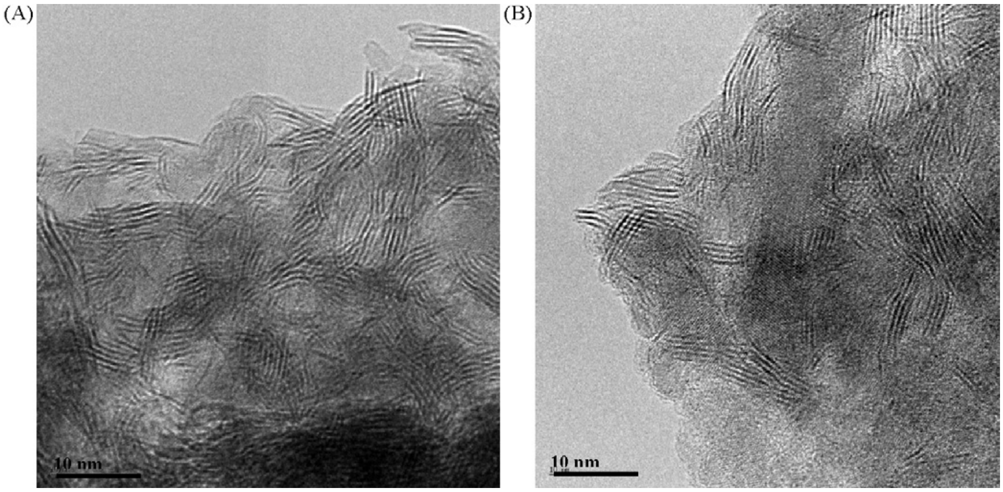

Fig. 5. High-resolution TEM images of unsupported NiMo sulfide catalysts prepared at difference H_2 pressure: (A) 2.1 MPa; (B) 3.4 MPa.

medium surface area of 161 m^2/g, while the catalyst prepared at 3.4 MPa has a much higher surface area (231 m^2/g). Thus, the NiMo sulfide catalyst with higher specific surface area and larger pore volume could be synthesized at higher preparation pressure.

Fig. 5 presents the HRTEM images of unsupported NiMo sulfide catalysts prepared at 350 °C under initial H_2 pressure of 2.1 and 3.4 MPa. Similar to Fig. 3, the fringes observed in the photographs are characteristic of slabs of crystalline MoS_2. According to the images, the relatively lower preparation pressure (2.1 MPa) leads to catalyst with lower average number of layers (2–6 layers, Fig. 5A) in the stacks, while the higher preparation pressure (3.4 MPa) leads to catalyst with higher average number of layers (4–14 layers, Fig. 5B) in the stacks. However, unlike the case of temperature effects (Fig. 3) discussed above, the change in the slab length was not apparent when preparation pressure was increased in this range. As shown in Fig. 5, the catalysts prepared at 2.1 and 3.4 MPa appear to show similar slab length of basal planes.

The product selectivity and HYD/DDS ratio results as shown in Table 1 are consistent with HRTEM results. In the pressure range of 2.1–3.4 MPa, the higher H_2 pressure can induce an increase of the number of stacked layers and resulted in lower hydrogenation selectivity, while lower average number of layers in the stacks can be induced by lower preparation pressure and leads to high hydrogenation selectivity. Therefore, it is likely that there exist more brim sites that are active for hydrogenation on the NiMo sulfide prepared at relatively lower pressure under the conditions employed.

3.2. Effects of organic solvent in catalyst preparation on HDS activity of NiMo sulfide catalysts

An organic solvent (decalin) was added to the aqueous solution of ATTM and Ni precursor and the effect of solvent amounts was investigated. Table 3 illustrates the effect of solvent amount used on the activity of resulting NiMo sulfide catalysts for the HDS of DBT and 4,6-DMDBT. Both the DBT and 4,6-DMDBT conversions increased significantly when the solvent added during the catalyst preparation was increased from 0 to 3 g. The NiMo sulfide catalyst prepared with 3 g organic solvent showed much higher activity for the HDS of DBT (73.5% conversion) and 4,6-DMDBT (59.3% conversion). For the DBT HDS, BP was predominant over the NiMo catalyst prepared without the solvent. With increasing the amount of solvent, however, the BP selectivity slightly decreased. Moreover, the selectivity of CHB became more significant than the BP selectivity. The similar trends were observed in the 4,6-DMDBT HDS. When the catalyst was prepared with higher solvent amount, the increase in the MCHT selectivity was more pronounced than that in the 3,3′-DMBP selectivity.

Table 4 presents the specific surface area and pore volume of unsupported NiMo sulfide catalysts prepared with and without

Table 3
Effect of organic solvent amount in catalyst preparation on simultaneous HDS of 4,6-DMDBT and DBT over unsupported NiMo sulfide catalysts at 2.8 MPa and 350 °C for 30 min (other catalyst preparation parameters: temperature = 350 °C, initial H_2 pressure = 2.8 MPa and Ni/(Mo + Ni) = 0.43).

Solvent amount(g)	0	1	3
DBT conversion (wt.%)	52.4	58.5	73.5
Selectivity (%)			
THDBT	7.7	6.2	3.4
BP	46.7	41.1	40.7
CHB	38.4	42.6	46.2
BCH	7.2	10.1	9.7
HYD/DDS[a]	1.1	1.4	1.5
4,6-DMDBT conversion (wt.%)	35.8	47.3	59.3
Selectivity (%)			
THDMDBT	46.2	37.8	31.0
3,3′DMBP	31.2	33.2	36.0
MCHT	20.9	27.0	31.1
DMBCH	1.7	2.0	1.9
HYD/DDS[b]	2.2	2.0	1.8
DBT/4,6-DMDBT conv ratio	1.5	1.2	1.2

[a] HYD/DDS = [selectivity to (THDBT + CHB + BCH)/selectivity to BP].
[b] HYD/DDS = [selectivity to (THDMDBT + MCHT + DMBCH)/selectivity to 3,3′-DMBP].

Table 4
Surface area and pore volume of fresh catalysts prepared at various solvent amount and Ni/(Mo + Ni) ratios (other catalyst preparation parameters: temperature = 350 °C and initial H_2 pressure = 2.8 MPa).

Solvent amount (g)	Ni/(Mo + Ni)	Surface area (m^2/g)	Pore volume (cm^3/g)
0	0.43	75	0.16
1	0.43	201	0.28
3	0.43	258	0.43
1	0[a]	320	0.72
1	0.20	245	0.39
1	0.33	207	0.28
1	0.50	187	0.25
1	0.56	159	0.21
1	1.0[b]	4	0.01

[a] MoS_2 alone without a promoter.
[b] NiS alone without Mo.

adding solvent. The results of BET analysis show that the NiMo sulfide catalyst prepared in the presence of solvent has much higher surface area (258 m^2/g) than that without solvent (75 m^2/g). The pore volume of catalyst also increased with increasing solvent amount. Therefore, it is clear that organic solvent addition in the preparation led to a highly active unsupported NiMo sulfide catalyst with high-surface area. Compared with the catalyst prepared without solvent addition, the catalysts prepared in the presence of organic solvent have larger surface area for gas–liquid–solid contact, and therefore more active hydrogen species (such as H atom) could be produced for the HDS reaction. This may partially rationalize much higher activity of the catalyst prepared with the organic solvent addition than the one prepared in the absence of the solvent.

The beneficial effect of organic solvent in this study is consistent with the results reported by Yoneyama and Song [18]. They reported that the addition of solvent in the preparation of MoS_2 from ATTM provided the high selectivity for cleavage of C–C bond and C–O bond and hydrogenation of naphthalene, and the addition of water led to much higher catalytic activity. The presence of the organic solvent helps to disperse ATTM-containing water droplet during preparation with vigorous agitation. This results a fine molecular dispersion of precursor molecules in the aqueous solution isolated by organic solvent. Afanasiev [29] also reported that the presence of organic matter decreased MoS_2 layer stacking and textural stabilization. In the present preparation procedure, the presence of organic solvent inhibits the crystallization of the sulfide. The role of the organic (hydrocarbon) solvent seems to be isolating and dispersing the droplets of aqueous solution containing precursor molecules dissolved in water before decomposition, facilitating the generation of catalytically active sulfide particles, and preventing the particle growth by reducing the stacking of layered sulfide slabs, as also suggested by XRD patterns of the catalysts (see later section).

3.3. Effect of Ni/(Mo + Ni) ratio on HDS activity of NiMo sulfide catalyst

Based on the above results on effects of preparation conditions, a series of unsupported NiMo catalysts were prepared with different Ni/(Mo + Ni) mole ratios at the same conditions of 350 °C and 2.8 MPa H_2 pressure with 1 g of organic solvent.

3.3.1. Specific surface area and structural properties

The BET specific surface areas of the unsupported NiMo sulfide catalyst are summarized in Table 4. Pore size distributions of Mo and NiMo sulfide catalysts are shown in Fig. 6. The surface area and pore volume of all catalysts were measured before the HDS reaction. The results showed that both Mo and NiMo sulfides are largely mesoporous with a bimodal pore structure. For comparison, the pore size distribution of CoMo sulfide prepared under the same condition is also shown in Fig. 6. The unsupported Mo sulfide catalyst prepared by hydrothermal method has a higher surface area and larger volume, with bimodal pore size distribution (two peak pore diameters around 3.8 and 6.2 nm). The surface area and pore volume of catalysts were reduced after addition of the promoter, but the bimodal pore size distribution is also apparent with the bimetallic sulfide catalysts with the two peak pore diameters (around 3.9 and 6.6 nm), as shown in Fig. 6. The decrease in surface area in sulfide catalyst after promoter addition for bimetallic sulfide catalysts was also reported by other researches [7,30]. They found that the surface area was decreased from 50 to 15–25 m^2/g after addition of promoter to Mo sulfide catalyst [31]. The surface area of unsupported Mo sulfide catalysts was affected by the Ni loading, which influenced the morphology and/or the degree of aggregation of the Ni–Mo phase. This results along with HDS data suggests that apart from the changes in number of active sites in the NiMo sulfide catalysts, the effectiveness of the active site may be enhanced.

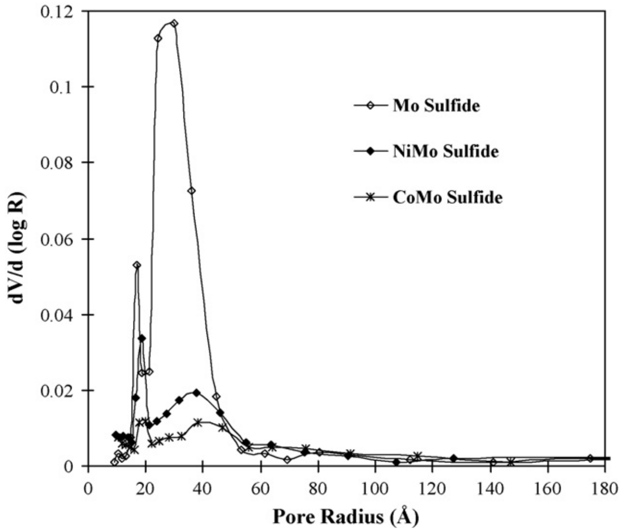

Fig. 6. Pore size distribution of unsupported Mo and NiMo sulfide catalysts. CoMo sulfide is also shown for comparison. Preparation parameters: temperature = 350 °C, initial H_2 pressure = 2.8 MPa, solvent amount = 1 g (Me/(Mo + Me) = 0.43, Me = Ni or Co for bimetallic sulfide samples).

The XRD patterns of the prepared NiMo sulfide catalyst series are shown in Fig. 7. Compared with a commercial MoS_2 powder, all unsupported Mo-based sulfide catalysts exhibited broad diffraction peaks, indicating a very poorly crystallized MoS_2 structure, particularly when the promoter was presented. The catalyst with the Ni/(Mo + Ni) ratio of 0.33 showed the diffraction peaks of poorly crystalline MoS_2, indicating that the MoS_2 maintains its structure in the presence of amorphous Ni, as reported earlier [32]. For the catalysts with the Ni/(Mo + Ni) ratio above 0.43, the diffraction peaks of the second metal sulfide appeared progressively. Ni_3S_4 was detected in the catalysts with the Ni/(Mo + Ni) ratio of 0.43, 0.50 and 0.56. Moreover, NiS was detected in the catalysts with the Ni/(Mo + Ni) ratio of 0.50 and 0.56. In most cases, the ternary Mo–Ni–S phases did not appear clearly. It is probably due to the fact that there is overlapping of diffraction peaks from MoS_2 and Mo–Ni–S phase. Another reason is that the active structures (Mo–Ni–S phase) are possibly presented as very small nano-crystallites, which cannot be characterized by X-ray diffraction method [33].

3.3.2. Catalytic activity and selectivity

Table 5 shows the effects of the Ni/(Mo + Ni) mole ratio on the HDS specific activity of unsupported NiMo sulfide catalysts. The Mo sulfide catalyst was prepared by the same procedure as NiMo sulfide catalysts, but without the Ni precursor. For the Ni sulfide catalyst, the same procedure was followed without the addition of ATTM, and CS_2 was used as sulfur source for sulfiding nickel [34].

A main purpose is to prepare catalysts with high activity in converting the refractory sulfur compounds such as 4,6-DMDBT that the conventional catalysts are not active enough to desulfurize efficiently. The catalytic activity results in Table 5 show clearly that the unsupported NiMo sulfide catalysts had a much higher HDS activity than the commercial alumina-supported NiMo catalyst (Cr424). Moreover, all unsupported NiMo sulfides and even the unpromoted MoS_2 catalysts show higher 4,6-DMDBT conversion than the commercial $NiMo/Al_2O_3$ catalyst.

Surprisingly, 4,6-DMDBT is slightly more reactive than DBT over the unsupported Mo sulfide prepared using ATTM without

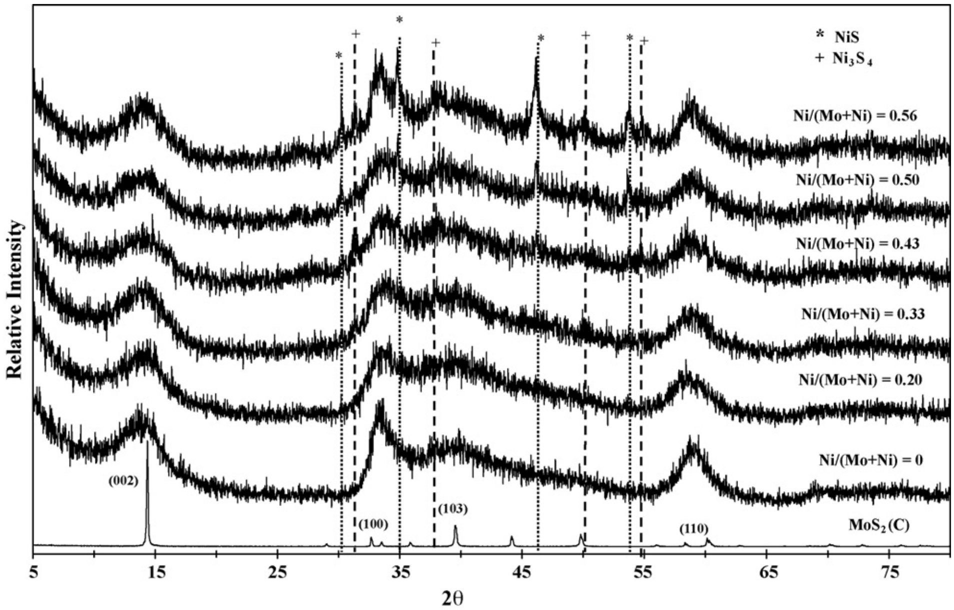

Fig. 7. XRD patterns of unsupported NiMo sulfide catalysts with various Ni/(Mo + Ni) ratios (MoS_2 (C) represents Aldrich MoS_2 reagent).

Table 5
Effect of Ni/(Mo + Ni) mole ratio on simultaneous HDS of 4,6-DMDBT and DBT over unsupported NiMo sulfide catalysts at 2.8 MPa and 350 °C for 30 min (other catalyst preparation parameters: temperature = 350 °C, initial H_2 pressure = 2.8 MPa, solvent amount = 1 g).

Catalysts	MoS_2	$NiMoS_2$					NiS	Cr424[a]
Ni/(Mo + Ni)	0	0.20	0.33	0.43	0.50	0.56	1	
DBT conversion (wt.%)	27.7	46.3	51.3	58.5	67.8	57.1	11.2	53.6
Selectivity (%)								
THDBT	44.5	10.1	7.0	6.2	4.2	6.4	26.5	4.0
BP	29.2	46.6	44.9	41.1	39.5	44.8	56.7	64.3
CHB	19.7	36.4	39.9	42.6	45.6	40.5	7.9	28.6
BCH	6.6	6.9	8.2	10.1	10.7	8.3	8.9	3.1
HYD/DDS[b]	2.4	1.1	1.2	1.4	1.5	1.2	0.8	0.6
4,6-DMDBT conversion (wt.%)	31.8	34.8	40.0	47.3	54.0	44.4	7.5	26.0
Selectivity (%)								
THDMDBT	87.1	45.0	45.4	37.8	33.9	42.1	84.6	40.6
3,3′-DMBP	7.8	26.6	26.3	33.2	33.4	31.2	10.7	32.6
MCHT	3.8	26.8	26.6	27.0	30.6	25.2	4.3	26.6
DMBCH	1.3	1.6	1.7	2.0	2.1	1.4	0.4	0.2
HYD/DDS[c]	11.8	2.8	2.8	2.0	2.0	2.2	8.4	2.1
DBT/4,6-DMDBT conv ratio	0.9	1.3	1.3	1.2	1.3	1.3	1.5	2.1

[a] Commercial alumina-supported NiMo sulfide catalyst.
[b] HYD/DDS = [selectivity to (THDBT + CHB + BCH)/selectivity to BP].
[c] HYD/DDS = [selectivity to (THDMDBT + MCHT + DMBCH)/selectivity to 3,3′-DMBP].

adding Ni (31.8% 4,6-DMDBT conversion vs. 27.7% DBT conversion). This was not expected initially but we have confirmed this trend by three duplicated experiments. This is mainly due to a higher activity of this unsupported and unpromoted MoS_2 for the HYD pathway which is the prominent for both sulfur compounds on this catalyst. As shown in Table 5, the HYD/DDS ratio of MoS_2 for both DBT and 4,6-DMDBT HDS was very high (2.4 for DBT HDS and 11.8 for 4,6-DMDBT HDS). The conversion of DBT and 4,6-DMDBT increased and reached maximum when Ni addition was increased up to the Ni/(Mo + Ni) ratio of 0.5. However, the conversion decreased when the ratio was further increased. These results indicated that there is a significant synergetic effect of Ni on the Mo catalysts for both DBT and 4,6-DMDBT HDS. The HYD/DDS ratio was above 1 for all catalysts even for the HDS of DBT for which the DDS pathway is generally predominant. It also indicated that the HDS of DBT and 4,6-DMDBT over unsupported Mo and NiMo sulfide catalysts mainly take the route of hydrogenation. The reactivity of 4,6-DMDBT relative to that of DBT is much higher on the unsupported Mo and NiMo sulfide catalysts compared to that over conventional alumina-supported NiMo sulfide catalysts, as can be seen from the ratio of DBT/4,6-DMDBT conversions shown in Table 5.

The HYD/DDS ratio decreased significantly when Ni was added into Mo sulfide catalyst. For example, for 4,6-DMDBT HDS, the HYD/DDS ratio is 11.8 with the Mo sulfide catalyst and 2.0 for the catalyst with the Ni/(Mo + Ni) ratio of 0.5. These results suggest that the promoting effect was largely due to the enhancement of DDS pathway, although HYD pathway is still a major pathway.

The remarkable increase in the catalytic activity by the addition of Co or Ni to Mo sulfide catalyst has been reported by many research groups. Upon increasing the concentration of the promoter atoms, the HDS activity may increase significantly. The other promoting effects may be highly dependent on the catalysts preparation procedure. The variation in the optimum Me/(Me + Mo) (Me = Co, Ni) mole ratios reported in the literatures may be explained. In the case of the unsupported catalyst, the optimum Me/(Me + Mo) atomic ratios are in the range of 0.3–0.54 for CoMo sulfide catalysts, [30,35,36] and from 0.4 to 0.55 for Ni–Mo sulfide catalysts [37,38]. In the case of supported catalyst, the optimum Me/(Me + Mo) atomic ratios is generally in the range from 0.2 to 0.4 for CoMo or NiMo sulfide catalysts [6,39]. In this study, the activity of the catalyst with the Ni/(Mo + Ni) ratio of 0.2 and 0.33 was much higher than MoS_2 and NiS sulfide catalysts. The NiMo sulfide catalyst with the Ni/(Mo + Ni) ratio of 0.50 showed the highest activity among all catalysts tested. This optimum Ni/(Mo + Ni) ratio agrees very well with the previous results reported for the unsupported NiMo sulfide catalysts.

During the catalyst preparation, the reaction between ATTM and $Ni(NO_3)_2$ leading to the bimetallic sulfide precursor was suggested as follows [7]:

$$2(NH_4)_2MoS_4 + Ni(NO_3)_2 \rightarrow (NH_4)_2\{Ni(MoS_4)_2\} + 2NH_4NO_3 \tag{1}$$

In the presence of hydrogen gas, the bimetallic sulfide is formed according to the reactions:

$$Ni(MoS_4)_2 + H_2 \rightarrow Ni(MoS_3)_2 + H_2S \tag{2}$$

$$Ni(MoS_3)_2 + H_2 \rightarrow Ni(MoS_2)_2 + H_2S \tag{3}$$

The chemical interaction between Ni and Mo atoms desired for effective NiMo catalysts implies that a good dispersion of the Ni promoter on MoS_2 is necessary for the formation of a large number of active NiMoS sites. Scanning tunneling microscope study by Lauritsen et al. revealed that the presence of Ni promoter atoms causes the change of the shape of the MoS_2 nanoclusters from triangular to hexagonally truncated structure [40]. Ni atoms may be located at the edge of MoS_2 crystallites to form Ni–Mo–S structure which is considered to be most active sites for HDS [6,41,42]. The hydrothermal method developed in our laboratory leads to the formation of very small size of NiMo sulfide cluster in the unsupported catalyst as shown by TEM in our present and previous work [19].

It is postulated that the organic solvent help to disperse and isolate the droplets of aqueous solution containing ATTM and Ni precursor under agitation which is heated rapidly to elevated temperatures of 300–375 °C (close to sub- and super-critical fluid conditions) under H_2 pressure, where ATTM reacts with the Ni precursor and decomposes to bimetallic sulfide species. Subsequently, very fine particles (nano-size) of NiMo sulfide catalyst are generated. Since Mo is surrounded by Ni in solution before and during hydrothermal decomposition under H_2, more Ni atoms would be incorporated into smaller Mo sulfide nano-crystallites to form more particles with NiMoS phases. From Table 5, the conversion of both sulfur compounds increased when the Ni/(Mo + Ni) atomic ratio was increased up to 0.5. This likely because, more active catalyst particles were formed with more Ni atoms, incorporated into the small nano-sized crystallites of Mo sulfide. However, for the catalyst with Ni/(Mo + Ni) atomic ratio above 0.5, excess Ni atoms may partly block the more active phase of NiMoS leading to decrease in the conversion of sulfur compounds. Although the separate phases of the Ni_3S_4 and NiS were detected for the catalysts with Ni/(Mo + Ni) ratio between 0.43 and 0.5 (Fig. 7), there was no apparent detrimental effect on the conversion of DBT and 4,6-DMDBT. What role does this separate Ni sulfide play is a matter of debate. If these metal (Ni and Co) sulfide particles are indeed catalytically active, they might help adsorb and dissociate hydrogen molecule. The resulting H species could attack the MoS_2 particles and create coordinatively unsaturated site at the edges [43,44]. However, it should note that excess Ni above the desired ratio to Mo decreased the catalytic activity significantly. Under elevated H_2 pressure, sulfur vacancy could be produced during the NiMo sulfide catalyst preparation stage and maintained during the hydrodesulfurization reaction. Therefore, the present results clearly demonstrate that the proper combination of Ni and Mo, not separate Ni sulfide, is responsible for higher catalytic activity.

4. Conclusions

The study of unsupported sulfide catalyst is a promising route for developing a better understanding and contributes to the development of better hydrotreating catalysts. Hydrothermal preparation of transition-metal sulfides is particularly interesting, because this method provides a highly active catalyst which does not require the sulfidation step. The unsupported NiMo sulfide catalysts synthesized from ATTM by the hydrothermal method exhibited the excellent catalytic activity for the simultaneous HDS of DBT and 4,6-DMDBT.

For the unsupported NiMo sulfide catalysts, the HYD pathway was predominant as compared with the DDS pathway in the HDS of DBT as well as the HDS of 4,6-DMDBT. The unsupported NiMo sulfide catalysts exhibit strong synergy between Mo and Ni for the HDS reaction. The maximum synergy in the HDS of DBT and 4,6-DMDBT was observed over catalyst with the Ni/(Mo + Ni) mole ratio close to 0.5.

The preparation conditions (temperature, H_2 pressure, and addition of an organic solvent to aqueous solution of Mo and Ni precursors) have a significant effect on the HDS activity and selectivity of unsupported NiMo sulfide catalysts. Both higher temperature and higher H_2 pressure in preparation led to higher surface area and larger pore volume and higher activity of the resulting NiMo sulfide catalysts for simultaneous HDS of DBT and 4,6-DMDBT.

However, the selectivity of NiMo sulfide catalysts was affected in different way. The NiMo catalyst prepared at higher preparation temperature became more selective for the HYD pathway but less selective for the DDS pathway for both DBT and 4,6-DMDBT HDS, as reflected by the increasing HYD/DDS ratio from 1.2 to 1.6 for DBT and from 1.5 to 2.9 for 4,6-DMDBT with increasing preparation temperature from 300 to 375 °C.

Increasing the initial H_2 pressure in catalyst preparation increased the activity of unsupported NiMo sulfide catalysts for both DBT and 4,6-DMDBT conversions, but the there are mixed effects on the selectivity. Initial increase in preparation pressure from 1.4 to 2.1 MPa enhanced HYD selectivity (increased HYD/DDS ratio); further increasing pressure to 2.8 and 3.4 MPa increased DDS selectivity but decreased HYD selectivity (decreased HYD/DDS ratio) for DBT HDS. For 4,6-DMDBT HDS, HYD/DDS ratio generally decreased with increasing preparation pressure from 1.4 to 3.4 MPa.

HRTEM revealed that the NiMo sulfide catalyst prepared at lower temperature (300 °C) had higher number of layers (6–10 layers) and long slabs and it showed lower hydrogenation activity. On the other hand, the NiMo sulfide catalyst prepared at higher temperature (375 °C) had lower number of layers (2–4 layers) and short slabs and it showed higher hydrogenation selectivity. For the unsupported NiMo sulfide catalysts prepared at 350 °C under initial H_2 pressure of 2.1 and 3.4 MPa, HRTEM revealed that the lower preparation pressure leads to catalyst with lower average number of layers (2–6 layers) in the stacks, while the higher preparation pressure leads to catalyst with higher average number of layers (4–14 layers) in the stacks. It is possible that the NiMo sulfide catalysts prepared at higher temperatures and/or at relatively lower pressures under the hydrothermal conditions in this work possess larger numbers of the brim sites (adjacent to the edge on the top layer of Mo-based sulfides) that have been recently discovered and shown to be active for hydrogenation by Topsoe, Besenbacher, Nørskov and their coworkers [26–28].

An organic solvent (decalin) addition in the catalyst preparation resulted in the highly active catalysts with higher surface area and larger pore volume. This suggests that the use of a hydrocarbon solvent help to isolate and disperse the droplets of aqueous solution containing ATTM and $Ni(NO_3)_2$ under agitation. This results a fine molecular dispersion of precursor molecules in aqueous solution which leads to the formation of nano-sized, highly active NiMoS catalyst particles. The hydrothermal method with suitable conditions leads to formation of nano-sized Mo sulfide clusters and more Ni atoms could be incorporated into smaller Mo sulfide nano-crystallites to form more active NiMoS catalysts.

The present study provides new insight into structure–activity–selectivity relationship and allows for controlling the catalyst selectivity as well as activity of unsupported NiMo sulfide catalysts by tailoring the hydrothermal preparation conditions.

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