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Synthesis and hydrodesulfurization performance of hierarchical mesopores alumina

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ABSTRACT

In the presence of sucrose, hierarchical mesopores alumina was prepared and used as hydrodesulfurization catalyst support. The pore structure and acidic property of the alumina can be easily controlled by pH value and concentration of precipitator. The physical and chemical properties of catalysts are apparently changed when this novel structure alumina are introduced as support. The interaction between active component and support is decreased. The Mo species are facilely reduced and there are less acid sites on the surface of the catalysts. The unique properties make this catalysts possess higher conversion and desulfurizing ratio for 4,6-DMDBT in this study.

1. Introduction

Hydrotreatment of heavy fractional oil has become major concern in refining. At present the key to hydrorefining of heavy fractional oil is to develop the most efficient catalyst. This kind of catalysts is entirely different from those for model molecules and middles distillate [1]. Cobalt or nickel promoted molybdenum or tungsten sulfides are well established as the active species for commercial hydrodesulfurization (HDS). In order to innovate the HDS catalysts, designing and synthesizing novel support have attracted much attention. Hierarchical mesopores/macropores support could decrease intra-diffusional resistance and simultaneously supply the reaction sites for different size of molecules.

Alumina is the most widely used hydrorefining catalysts support owing to its attractive mechanical properties and adjustable surface properties [2]. While the small surface area, broad pore distribution, and particularly intra-diffusional properties will be critical for its use in hydrotreating processes for heavy fractional oil. The synthesis of alumina with high surface area and hierarchical mesopores/macropores is the key issue to develop effective catalyst for this processes. Despite the fact that mesoporous alumina with various diameter and larger surface area have been prepared via non-ionic or electrostatic templating strategies [3–7], the samples merely exhibit mono-modal pore which cannot simultaneously supply sites for different size of molecules to react and intra-diffuse. Of pity is alumina with hierarchical mesopores/macopores was very recently achieved and synthesis approaches have been seldom reported [8–9]. It is necessary to pay more attention to synthesizing the alumina with this novel pore structure by tuning the synthesis routes and controlling preparation conditions.

2. Experimental

2.1. Preparation of alumina and catalysts

Alumina was synthesized via hydrothermal method using ammonium carbonate as precipitator in the presence of the sucrose and polyethylene glycol (PEG). Firstly, the aluminum nitrate was dissolved in sucrose aqueous solution with stirring, followed by the addition of PEG solution. After further stirring for a certain time, the solution of ammonium carbonate was introduced. The reaction product was transferred to the autoclave, and aged at 100 °C for 24 h. As synthesized sample was washed with deionized water and dried at 60 °C for 48 h. Finally, the product was calcined at 600 °C for 4 h with ramp rate of 2 °C min^{-1}.

The CoMo/Al_2O_3 catalysts with a mass ratio of 4/15/81 were synthesized via impregnation method using calcined alumina as the support. Cobalt nitrate and ammonium molybdate are respectively the promoter and active component precursor. These catalysts are denoted as CoMo/Al_2O_3-*x* (*x* is number from 1 to 4). For comparison, CoMo/Al_2O_3 catalyst with the same composition as above was prepared using the commercial alumina as support. This catalyst is named as CoMo/Al_2O_3.

2.2. Characterization of alumina and catalysts

Nitrogen sorption isotherms of samples were obtained by a Micromeritics TriStar 3000 analyzer at 77 K. Before any measurements were taken, the samples were degassed at 350 °C for 12 h under vacuum. The BET surface area was calculated using experi-

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mental points at a relative pressure of $P/P^0 = 0.05–0.25$. The pore size distribution was calculated by the BJH method. XRD was performed on a X'Pert PRO MPD powder diffractometer, using Ni-filtered Cu Kα radiation with a tube voltage of 45 kV, a tube current of 40 mA and scanned from 10° to 75° (2θ). TEM images were obtained by Philips CM200 electron microscope. The powder samples for the TEM measurements were suspended in ethanol and then dropped onto copper grids with porous carbon films.

The reducibility of the metal species was analyzed using temperature-programmed reduction (TPR) on chem-adsorption analyzer (ChemBET 3000, Quantachrome, USA) with a ramp rate of 10 °C min^{-1} under flowing 10% H_2 in Ar.

The acidic property of the catalysts was monitored by temperature-programmed desorption (TPD) on chem-adsorption analyzer (ChemBET 3000, Quantachrome, USA) using ammonium as adsorbate. The catalyst was firstly degassed at 500 °C for 1 h and then adsorbed ammonium for 1 h. It was performed at a ramp rate of 10 °C min^{-1} under flowing 10% NH_3 in Ar. The acid type was determined on inferred photography (Magna IR 750, Nicolet, USA) using pyridine as probe molecule.

2.3. *Catalyst activity test*

The hydrodesulfurization performance of the catalysts was evaluated in a high pressure micro-reactor using 4,6-dimethyldibenzothiophene (4,6-DMDBT) as model compound. Typically, 5 g catalyst was introduced to the reactor. Prior to reaction, the fresh catalyst was sulfurized with CS_2 at 300 °C for 6 h under 2 MPa hydrogen pressure. Then the 4,6-DMDBT with concentration of 0.5% (wt%) soluted in the toluene was introduced under H_2/Oil ratio of 300/1 (v/v) and LHSV of 2 h^{-1}. After reaction at 260 °C for 5 h the product was poured out and analyzed by gas chromatography (Agilent 6820) and mass photography (Agilent 5973N/6890).

3. Results and discussion

3.1. *Alumina characterization*

The nitrogen adsorption–desorption isotherms and pore distribution of the alumina are shown in Fig. 1. There are two hysteresis loops in the isotherms, which is consistent with hierarchical mesopore distribution. The pores with the smaller size bear concentrate distribution; on the contrary, with the larger size possess broad distribution. This difference is attributed to various pore formation mechanisms. The smaller pore is produced via non-ionic templating route. Aluminum species can be connected with hydroxyl of sucrose or PEG via hydrogen bond, which results in the formation of mesostructure of inorganic and organic. After the mesostructure is calcined, the pore with concentrate distribution can be exhibited. The pore with larger size is determined by $NH_4Al(OH)_2CO_3$ that is an intermediate product in the synthesis of the alumina. During the calcination of mesostructure, $NH_4Al(OH)_2CO_3$ can be decomposed and give off the gases such as CO_2, NH_3 and H_2O. The diameter of some primary smaller mesopores is broadened owing to the release of these gases. The investigation showed that the more amount of $NH_4Al(OH)_2CO_3$ was formed in the mesostructure, the more larger pores could be obtained. Of note is that pH value of synthesis system should be controlled above 9.0 if $NH_4Al(OH)_2CO_3$ can be produced. In addition, the pore structure of alumina (shown in Table 1) can be easily tuned by controlling synthesis conditions such as amount of sucrose, crystallizing temperature and pH value. The larger pore volume can be obtained at high temperature and high pH value. The higher H_2O/Al ratio can contribute more mesopore with larger pore diameter to the alumina. While the pore with concentrate pore distribution can be shown when the samples are synthesized at higher concentration of structure directors. Of note is the surface area of most synthesis alumina is smaller than the commercial one, while they bear the larger pore volume and hierarchical mesoporous distribution.

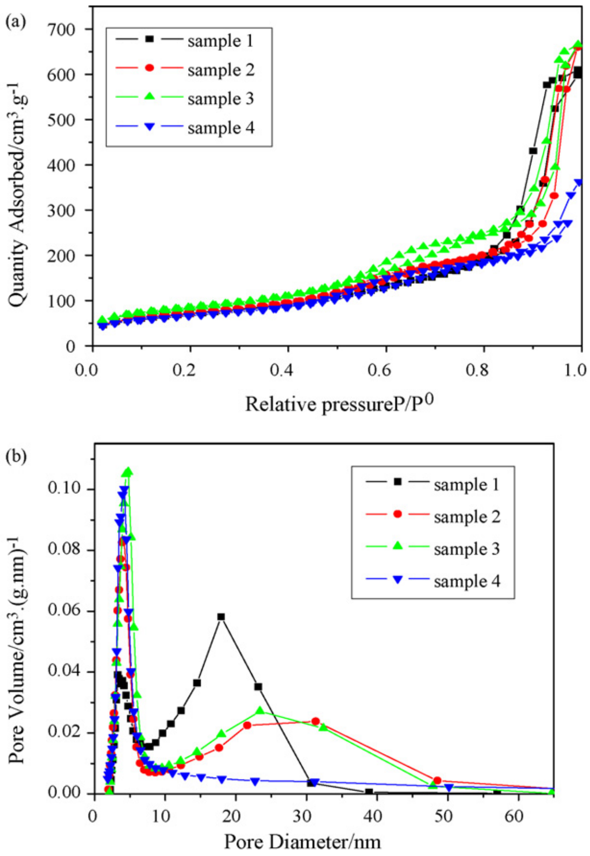


Fig. 1. (a) Isotherms and (b) pore distribution of alumina.

Fig. 2 shows X-ray diffraction (XRD) patterns of as-synthesized and calcined products. The as-synthesized samples prepared at pH value of above 9.0 bear mixture phase of $NH_4Al(OH)_2CO_3$ and boehmite (AlOOH), and under 9.0 possess pure boehmite phase. Of note is that all the samples calcined at 600 °C are transformed to the phase of γ-Al_2O_3. The weak and broad diffraction peaks in Fig. 2b

Table 1
Surface area and pore structure of the samples calcined at 600 °C.

Sample	Surface area/m^2 g^{-1}	Pore diameter/nm		Pore volume/cm^3 g^{-1}
		Smaller	Larger	
1	251.4	3.3	17	0.941
2	257.9	4.0	28	1.020
3	301.2	4.6	26	1.029
4	235.7	4.0	–	0.556
Commercial alumina	330	6.48	–	0.87

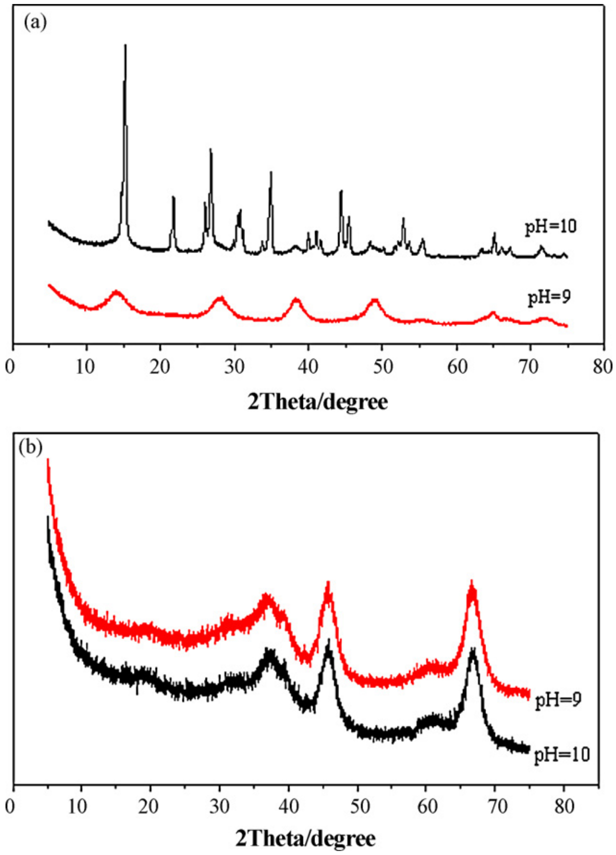


Fig. 2. XRD patterns of (a) as-synthesized and (b) calcined products.

demonstrate that the samples are composed of small crystals with a crystalline size in nanometer scale. Low-angle diffraction patterns of the sample exhibit a broad peak between 1° and 3° of 2θ that is characteristic of a disordered mesostructure. This is in agreement with the formation mechanism of mesopore in this study.

Fig. 3 indicates that acidic property of the samples can be easily tuned by controlling the synthesis conditions, particularly pH value. The samples synthesized under different conditions exhibit different amount of acid and acid strength. The weak and medium strong acid sites can be simultaneously shown in all the catalysts. The amount of medium strong acid is increased with the decrease of pH value. It means that aluminum atom in the alumina prepared with ammonium carbonate as precipitator at low pH value is mainly in six-coordination state.

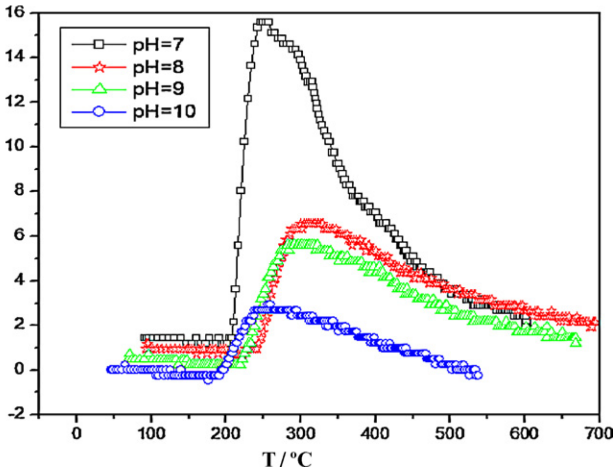


Fig. 3. NH_3-TPD spectra of alumina prepared at different pH value.

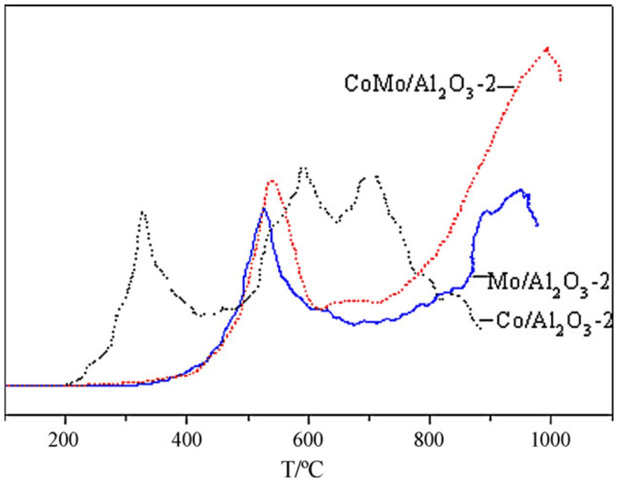


Fig. 4. TPR spectra of catalysts with different composition.

3.2. Catalyst characterization

Fig. 4 gives TPR data of the catalysts with different composition. Three peaks are shown for Co/γ-Al_2O_3-2. The peak of 340 °C is characteristic of reduction of Co_3O_4. The middle peak (600 °C) corresponds to reduction of surface Co^{2+} and the peak of 700 °C is ascribed to Co^{2+} occupying vacancies of octahedron γ-Al_2O_3. There are two parently reduction peaks for Mo/γ-Al_2O_3-2 and CoMo/γ-Al_2O_3-2. The former peak is signal of reduction of Mo in eight-coordination (Mo^{6+}(O)) and latter is in four-coordination (Mo^{6+}(T)). The spectra indicate that Mo^{6+}(O) over the monometallic catalyst is easily reduced. The reduction temperature is significantly decreased from about 550 °C of bimetallic catalyst to 500 °C of monometallic. It means that there is intimate interaction between Co and Mo species. The interaction is so strong that reduction peaks of Co_3O_4 all disappear for bimetallic catalysts. It demonstrates that cobalt species have limited reducibility because this interaction enhances diffusion capacity of cobalt ion into the structure of alumina to impede the reduction. The interaction between active component and support is decreased owing to this strong interaction between Co and Mo. It can be seen from the decrease of the reduction temperature of Mo^{6+}(O) over bimetallic catalyst compared to monometallic. In addition, the considerable difference in reduction temperature is demonstrated for pure and supported MoO_3. The transformation temperature of pure MoO_3 to MoO_2 is 725 °C, which is far higher than 550 °C of supported MoO_3. This is because that polarization of Al^{3+} to the terminal oxygen of MoO_3 results in the easy reduction of Mo species.

TPR spectra of catalysts prepared with different synthesis alumina are given in Fig. 5. The data exhibit that reduction temperature of Mo^{6+}(O) is almost identical for different catalysts, however, the reduction amount is different. The highest amount of reduction is assigned to CoMo/γ-Al_2O_3-1 and the lowest to CoMo/γ-Al_2O_3-2. The investigation demonstrated that the increased order of reduction amount of the Mo^{6+}(O) is consistent with the increased order of the pore diameter of the catalyst. The facile reduction of active component may be ascribed to the decrease of the intra-diffusional resistance and then contribute to the higher performance of the reactivity of the catalysts.

The acidic properties of the catalysts were respectively determined by IR and TPD technologies. The acid type was monitored by IR using pyridine as probe molecule. The IR spectra shown in Fig. 6a

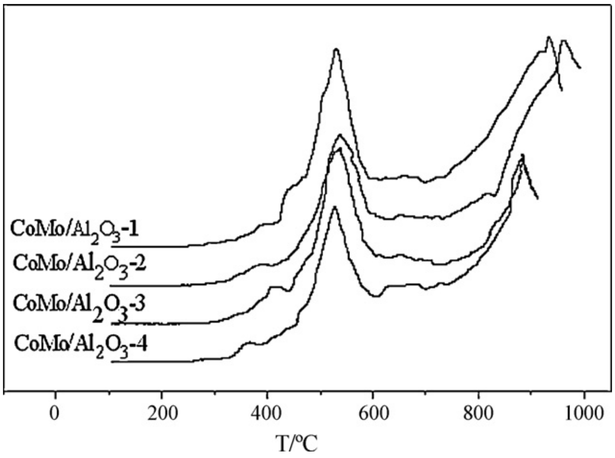


Fig. 5. TPR spectra of catalysts prepared with different alumina.

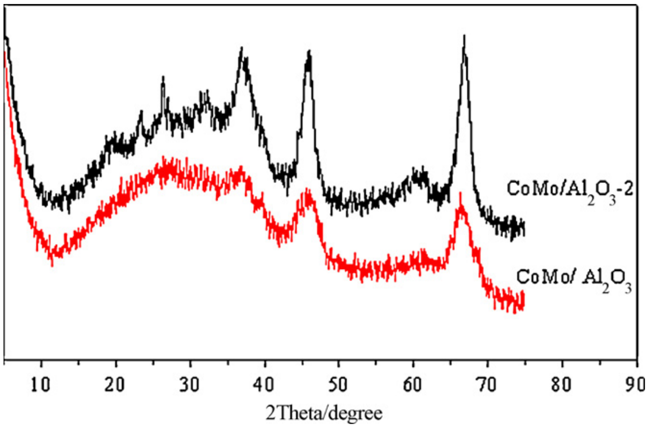


Fig. 7. XRD patterns of catalysts prepared with different alumina.

indicate that there are more Lewis acid sites compared to Bronsted in all the catalysts. Whereas the total acid amount of the catalysts prepared with synthesis alumina is clearly less than that prepared with commercial alumina. NH_3-TPD spectra are shown in Fig. 6b. It further demonstrates the above phenomenon for the amount of total acid. Of note is that the catalysts prepared with synthesis alumina bear more weaker acid sites. The report indicated that high performance catalyst for desulfurization of alkyl-substituted DBT should possess larger amount of Lewis acid sites as well as more weak acid sites [10]. This is because that HDS of alkyl-substituted DBT may firstly result in hydrogenation to saturate aromatic ring or split ring, which may decrease space resistance for successively desulfurization. The hydrogenation pathway is actively facilitated by Lewis acid. Bronsted acid can also accelerate hydrogenation, but present more severe side effects as coke formation compared to Lewis acid [11]. The acid sites with stronger acid strength can apparently encourage condensation reaction and then result in the severe catalyst deactivation due to deposition of coke. The above data show that the acidic properties of the catalysts prepared with the synthesis alumina will be beneficial to the desulfurization of alkyl-substituted DBT.

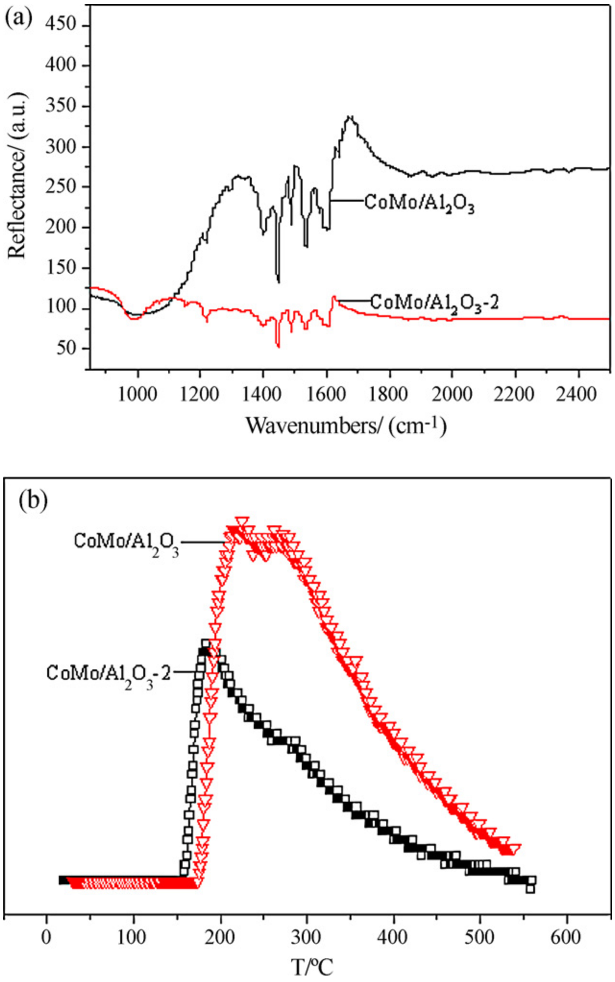


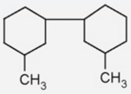
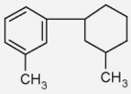
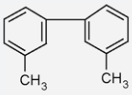
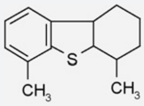
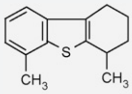
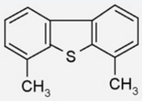
Fig. 6. Acidic property of the catalysts prepared with different alumina: (a) pyridine-IR and (b) NH_3-TPD.

The XRD patterns of the catalysts shown in Fig. 7 indicate that there are no diffraction lines of Mo species for CoMo/Al_2O_3. It means that the Mo species are well dispersed on the support. Whilst for catalyst prepared with synthesis alumina, very small diffraction peaks of $CoMoO_4$ are detected at 23°, 26°, 32° and 33°. This phenomenon is responsible for weak Mo–support interaction or acidification [12]. Besides the peaks corresponding to γ-Al_2O_3 and $CoMoO_4$, the signals of crystalline MoO_3 are also exhibited at 23° and 27°. The higher dispersion of the Mo species over CoMo/Al_2O_3 is ascribed to the higher surface area of commercial alumina compared to the synthesis one. The figure further shows that relative crystallinity of synthesis alumina is higher than the commercial support.

3.3. *Catalytic performance of catalysts*

The results of typical product distribution over different catalysts are listed in Table 2. It indicates that the dominant pathway of HDS for all the catalysts in this study is via hydrogenation route. This is due to methylcyclohexyltoluene (MCHT) and 3,3′-dimethylbiphene (3,3-DMBP) are respectively major products of the hydrogenation route and direct desulfurization pathway [13–15]. The amount of MCHT is far higher than that of 3,3-DMBP. The conversion and desulfurizing ratio of 4,6-DMDBT shown in Fig. 8 are almost identical using the catalysts prepared with synthesis alumina. Whereas for the commercial alumina as support, the conversion is significantly higher than the desulfurizing ratio and is much lower than that of the synthesis alumina as support. Using the catalyst of CoMo/Al_2O_3-1, the conversion and desulfurizing ratio for 4,6-DMDBT can be all up to 99.4%. This desulfurizing ratio is higher than previously reported when the CoMo/Al_2O_3 acted as catalyst under moderate reaction conditions [15–17].

Table 2
Product distribution for HDS of 4,6-DMDBT over different catalysts.

Products molar ratio/%	$CoMo/Al_2O_3$	$CoMo/Al_2O_3$-1	$CoMo/Al_2O_3$-2	$CoMo/Al_2O_3$-3	$CoMo/Al_2O_3$-4
 and its isomer	–	6.77	2.4	2.84	1.89
 and its isomers	0.53	91.02	84.61	89.67	91.58
	0.24	1.58	1.88	1.66	1.65
 and its isomer	52.55	–	–	–	–
 and its isomer	18.37	–	0.82	–	–
 and its isomer	27.81	0.63	5.26	0.99	1.48

4. Discussion

In the presence of sucrose and PEG, hierarchical mesoporous alumina can be synthesized via hydrothermal method using ammonium carbonate as precipitator. The formation of smaller mesopore may attribute to the interaction between the organic and inorganic species, which contributes the space pore to the alumina. The formation of larger mesopore is attributed to the decomposition of $NH_4Al(OH)_2CO_3$. The hot gas released from the decomposition can extend the primary smaller mesopore. It means that the $NH_4Al(OH)_2CO_3$ should be obtained if the larger mesopore can be exhibited in the alumina. Herein the pH value of the synthesis system should remain above 9.0 to produce $NH_4Al(OH)_2CO_3$. In addition to the amount of $NH_4Al(OH)_2CO_3$, the pore structure can be modulated by other synthesis conditions. The larger pore diameter and pore volume can be shown when the sucrose and PEG are simultaneously introduced to the synthesis system as well as the samples are prepared under the higher crystallizing temperature or higher pH value. In addition, there is some nanorod structure comprised in the particle catalysts as shown in Fig. 9. It has been

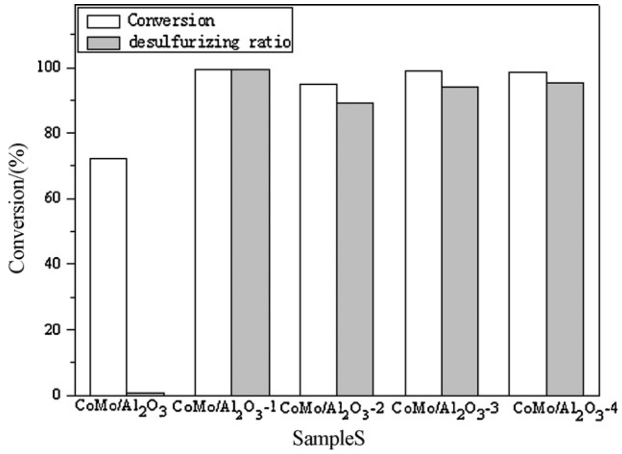


Fig. 8. Conversion and desulfurization ratio of 4,6-DMDBT over different catalysts.

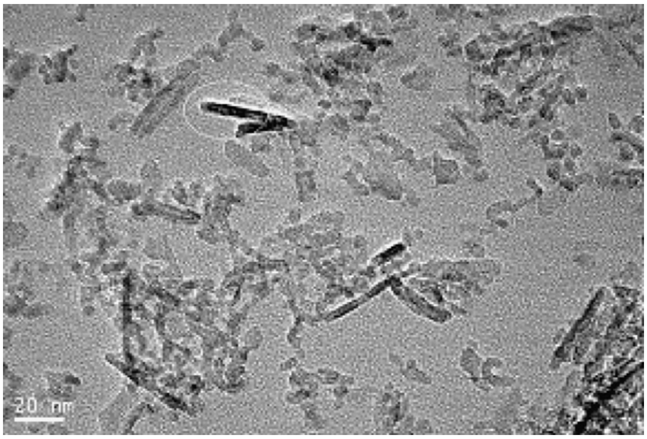


Fig. 9. TEM image of the $CoMo/Al_2O_3$-1 catalyst.

proposed that the HDS of 4,6-DMDBT is a structure-sensitive reaction [18]. The nanorod structure may contribute small-size effect, surface effect and good thermal stability to the catalysts [19]. The effect of this special structure on the reaction performance of the catalysts will be investigated in the future.

It has been proposed that the hydrorefining catalysts for heavy fractional oil should bear larger surface area [20]. Of note is that the surface area is not crucial factor in this study. The surface area of CoMo/Al_2O_3 is 284 m^2/g, which is much larger than that of 164 m^2/g for CoMo/Al_2O_3-1. The reaction results showed that the CoMo/Al_2O_3-1 possessed much higher HDS activity compared to CoMo/Al_2O_3. Shape-selective effect is exhibited during the HDS of 4,6-DMDBT. The mesopore diameter from 7 nm to 10 nm is beneficial to sulfur removal. The desulfurizing ratio is directly proportional to the pore volume. The higher performance of the catalysts is determined not only by the pore structure, but also by the amount of reduced active composition. The more reduced Mo species on the surface of the catalysts, the higher the HDS activity is. Certainly, the HDS performance is also correlation to the acidic properties of the catalyst. It has been proved that the interaction between metallic particles and acid sites in the support induces the formation of electron deficient metallic particles, which influences the HDS performance of the catalysts [21]. The acidic properties of CoMo/Al_2O_3-*x* is considerably different from that of CoMo/Al_2O_3. There are more Lewis acid sites on the surface of CoMo/Al_2O_3-*x*, which can induce more electron deficient sites over active component. It then may contribute high HDS activity to the CoMo/Al_2O_3-*x*.

5. Conclusion

Using ammonium carbonate as precipitator, hierarchical mesoporous alumina can be obtained by turning the synthesis conditions, particularly pH value of synthesis system. The introduction of alumina with hierarchical mesopore as catalyst support for 4,6-DMDBT desulfurization can significantly change its physical structure and properties thus improving its catalytic performance. To design the catalyst with high HDS activity, more attention should be paid to its pore structure, acidic and reduced properties.

Acknowledgements

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