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Design and Synthesis of Metal Sulfide Catalysts Supported on Zeolite Nanofiber Bundles with Unprecedented Hydrodesulfurization Activities

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Supporting Information Placeholder

ABSTRACT: Developing highly active hydrodesulfurization (HDS) catalysts is of great importance for producing ultra-clean fuel. Herein, we show crystalline mordenite nanofibers (NB-MOR) with bundle structure containing parallel-mesopore channels. After introducing cobalt and molybdenum (CoMo) species in the mesopores and micropores of NB-MOR, the NB-MOR supported CoMo catalyst (CoMo/NB-MOR) exhibits an unprecedented high activity (99.1%) as well as very good catalyst life in the HDS of 4,6-DMDBT, compared with a conventional γ-alumina-supported CoMo catalyst (61.5%). The spillover hydrogen formed in the micropores migrates onto nearby active CoMo sites in the mesopores, which could be responsible for the great enhancement of HDS activities.

Increasingly stringent environmental legislation is pressuring manufacturers to reduce the sulfur content in gasoline and diesel fuel to a level of 10 ppm and lower.[1] To reach this low sulfur level, even highly refractory sulfur compounds in the fuel, such as 4,6-dimethyldibenzothiophene (4,6-DMDBT), must be almost completely removed.[2] Generally, conventional hydrodesulfurization (HDS) catalysts, γ-alumina-supported metal sulfides (CoMo/γ-Al_2O_3 or NiMo/γ-Al_2O_3), have difficulty to fully remove 4,6-DMDBT due to steric hindrance by the methyl groups adjacent to the sulfur atom.[3] One of the solutions for this problem is to increase the hydrogenating ability by replacing the metal sulfides by noble metals.[4] However, the relatively short catalyst life and high cost of these noble metals strongly limit their applications.[5]

It has been reported that hydrogen spillover can greatly enhance the hydrogenating ability;[6] thus, an improvement of the hydrogen spillover ability for conventional HDS catalysts would facilitate very high HDS activities.[7] Thanks to recent successful syntheses on mesoporous zeolites,[8] it should be possible to design catalytic active sites in micropores and mesopores of mesoporous zeolites that have hydrogen spillover ability and hydrogenating ability, respectively.

Herein, we first report a facile method to synthesize nanofiber bundles of zeolite MOR (NB-MOR). The resulting material has parallel-mesopore channels in the nanofiber bundles of the microporous MOR zeolite. In addition, after introducing cobalt and molybdenum species in the mesopores and micropores, followed by sulfidation, the NB-MOR supported CoMo catalyst (CoMo/NB-MOR) exhibits an unprecedented high activity in the HDS of 4,6-DMDBT, compared with conventional CoMo(NiMo)/γ-Al_2O_3 catalysts. This feature may be attributed to

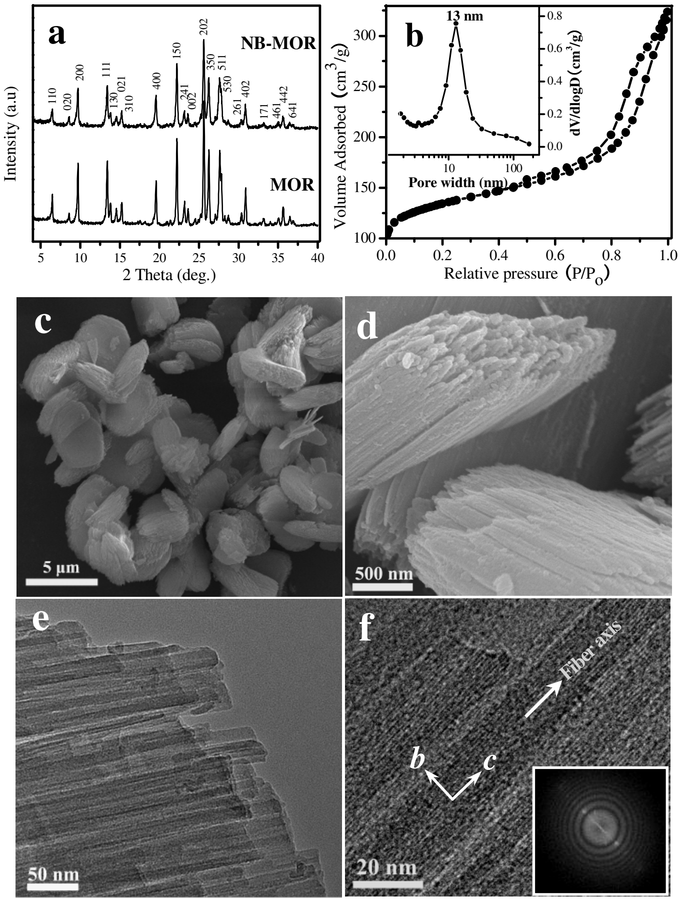

Figure 1. (a) XRD patterns, (b) N_2 adsorption isotherm, (c) low resolution SEM image, (d) high resolution SEM image, (e) low resolution TEM image and (f) high resolution TEM image (Fast Fourier Transform (FFT) inset.) of NB-MOR sample.

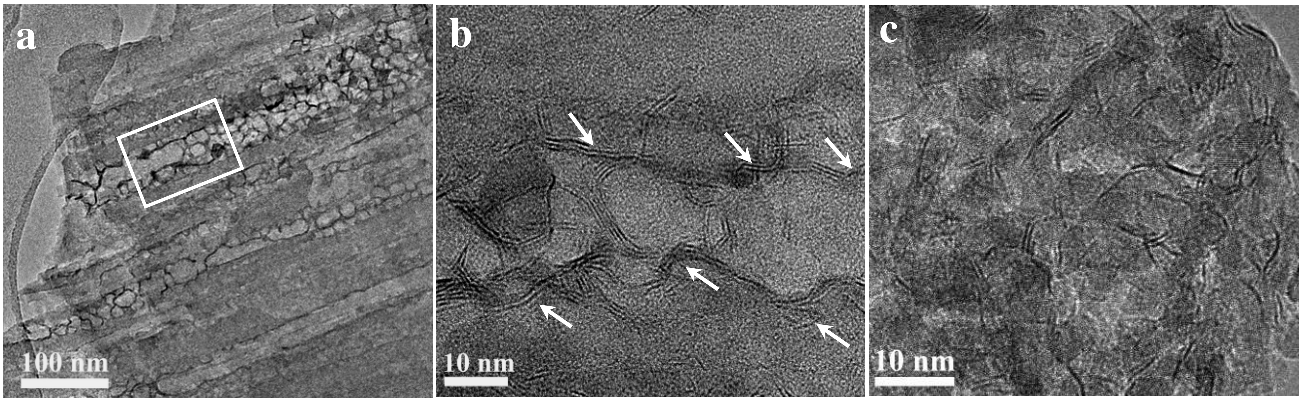

Figure 2. (a) Low resolution TEM image of the sulfided CoMo/NB-MOR catalyst. (b) High resolution TEM image in the selected area in Figure 2a marked by white square. (c) High resolution TEM image of the sulfided CoMo/γ-Al_2O_3 catalyst.

the migration of spillover hydrogen formed in the micropores onto nearby active CoMo sites in the mesopores, which significantly enhances the hydrogenating ability of the catalyst. This catalyst design concept provides a new strategy for the rational preparation of multi-functional highly active catalysts.

Despite the recent successful synthesis of nano-sized zeolite materials, such as nanosheets and nanoparticles by using mesoscale organic templates,[9] it is difficult to obtain zeolite nanofibers by the similar route. In this work, we synthesized a random cationic copolymer containing quaternary ammonium groups and used it as a template for the synthesis of mordenite zeolite nanofibers, which can be assembled to a bundle structure (see section S1 in the Supporting Information).

Figure 1 shows the X-ray diffraction (XRD) pattern, nitrogen isotherm, scanning electron microscopy (SEM) images, and transmission electron microscopy (TEM) images of NB-MOR. The XRD pattern shows well-resolved peaks in the range 4-40°, which correspond to the MOR zeolite structure (Figure 1a). The nitrogen sorption isotherm of NB-MOR exhibits a hysteresis loop at a relative pressure of 0.45-0.96, which is typically assigned to the presence of mesostructure (Figure 1b). Correspondingly, the mesopore-size distribution of the NB-MOR is mainly centered at 13 nm (insert, Figure 1b). Sample textural parameters are presented in Table S2. The SEM images (Figure 1c,d) reveal that NB-MOR has a particle size of 3×5 μm. The NB-MOR particles consist of parallel zeolite nanofibers (Figure 1d-f). The zeolite nanofibers have diameters ranging from 10-30 nm and these nanofibers aggregate into bundles. In this manner, parallel-mesoporous channels are formed in the aggregated bundles (Figure S2). Furthermore, fast fourier transfrom (FFT) of the NB-MOR TEM image (insert in Figure 1f) shows that the *b*-axis of MOR (010 face, pore size at 3.4 × 4.8 Å) is perpendicular to the mesopore direction. This micro-mesopore structure feature could be beneficial for the mass transfer of small molecules such as hydrogen from micropores to mesopores.

In catalyst preparation, the aim is to disperse the active metal species not only in the mesoporous channels but also in the micropores of the NB-MOR. To introduce the active metal species into the support micropores, the pH of the impregnation solution was adjusted to about 10.0. In this case, most of the $Mo_7O_{24}^{6-}$ is converted to small MoO_4^{2-} species,[10] which easily penetrate into the micropores of NB-MOR. After sulfidation by a mixture of H_2 and H_2S (400 °C, 10 vol% H_2S), the $CoMoS_2$ phases (marked by white arrows) are uniformly located in the parallel mesopore channels of the NB-MOR (Figure 2a and 2b). Moreover, very small metal sulfide clusters may be formed in the micropores of zeolite. This suggestion is confirmed by additional TEM images and X-ray energy dispersive spectroscopy (EDS) analysis of a thin-sectioned sulfided microporous Mo/MOR catalyst sample, as shown in Figures S3-S6. The TEM images

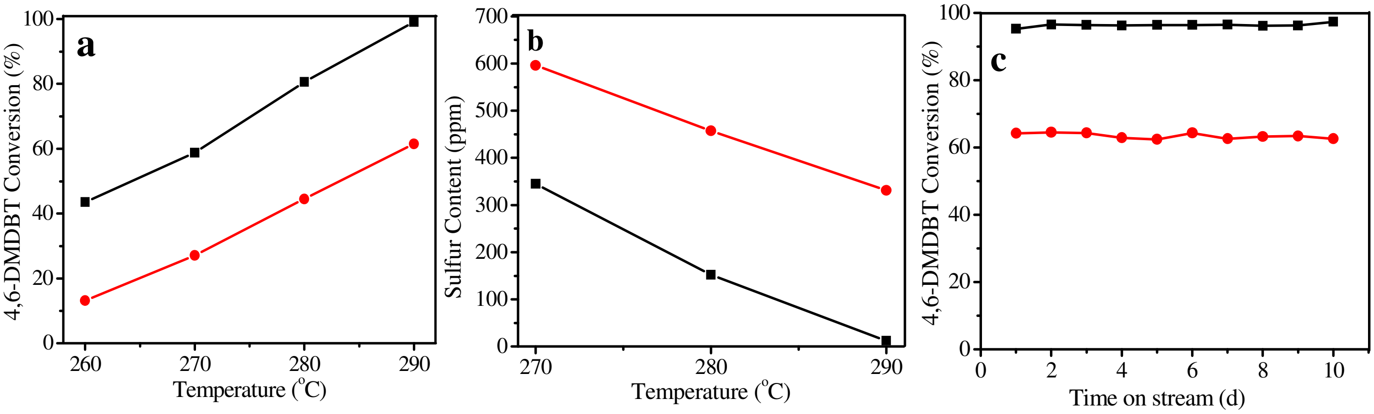

Figure 3. The catalysts activities. (a) 4,6-DMDBT conversion and (b) the remaining sulfur content in the reaction products at different temperatures over (■) CoMo/NB-MOR and (●) CoMo/γ-Al_2O_3 catalysts. (c) Dependence of the 4,6-DMDBT conversion on reaction time over (■) CoMo/NB-MOR and (●) CoMo/γ-Al_2O_3 catalysts. (Reaction conditions: total pressure, 5.0 MPa; temperature, 290 ºC; feed stock, 0.5 wt.% 4,6-DMDBT in decalin; WHSV of feed solution is 14.6 h^{-1}; H_2/oil = 700 Nm^3/Nm^3. The two catalysts have the same metal loading, the molar ratio of Co/Mo was 1:2, and the Mo loading was 10.7 wt.%).

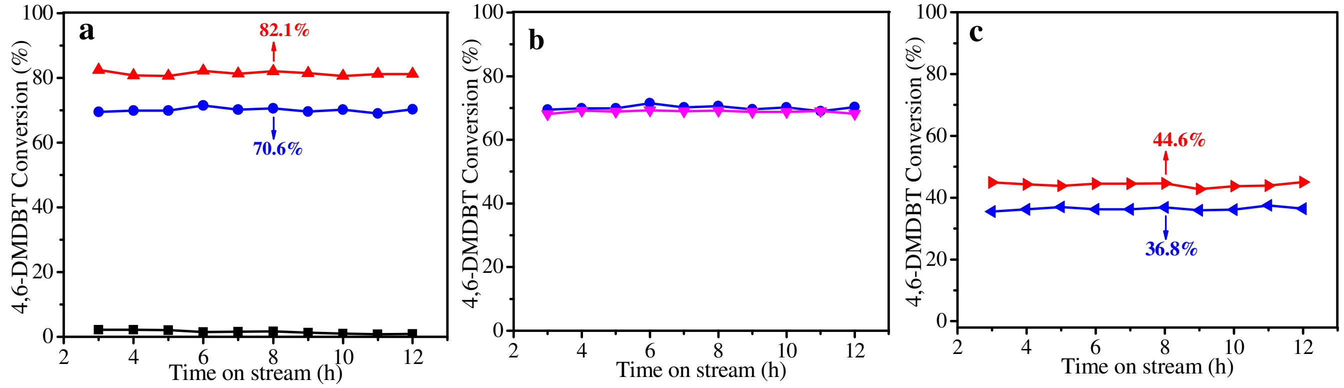

Figure 4. Dependences of the 4,6-DMDBT conversion on the reaction time over series catalysts on the hydrogen spillover experiments. (a) (■) 0.2 g CoMo/MOR (2.7 wt.% Mo), (●) 0.3 g CoMo/NB-MOR (12.5 wt.% Mo) and (▲) 0.3 g CoMo/NB-MOR (10.7 wt.% Mo) mixed with 0.2 g CoMo/MOR (2.7 wt.% Mo). (b) (●) 0.3 g CoMo/NB-MOR (12.5 wt.% Mo) and (▼) 0.3 g CoMo/NB-MOR (12.5 wt.% Mo) mixed with 0.2 g MOR. (c) (◀) 0.3 g CoMo/γ-Al_2O_3 (12.5 wt.% Mo) and (▶) 0.3 g CoMo/γ-Al_2O_3 (10.7 wt.% Mo) mixed with 0.2 g CoMo/MOR (2.7 wt.% Mo). For all catalysts the molar ratio of Co/Mo was 1:2.

(Figures S3 and S4) of a selected zone of the microporous Mo/MOR catalyst sample show that the catalyst only contains micropores and that no larger MoS_2 nanoparticles can be observed. However, the EDS element mapping of the selected zone confirms the presence of Mo and S (Figure S5); the atomic Mo/S ratio is about 0.88 (Table S3). Therefore, it is suggested that only very small metal sulfide clusters (MoS_x, $1<x<2$) are highly dispersed in the micropores of zeolite MOR. Interestingly, after destruction of the ordered micropores by the strong electron beam, larger nanoparticles (1-2 nm) were observed (Figure S6). The large nanoparticles are attributed to the aggregation of the very small metal sulfide clusters. These results also support that the micropores of the Mo/MOR catalyst sample contain very small metal sulfide clusters. It is worth noting that results published previously show that very small metal sulfide clusters such as Ni-Mo-S and MoS_x could be dispersed inside the micropores of zeolite Y and ZSM-5.[11] The authors also suggested that the MoS_x or Ni-Mo-S clusters inside the zeolite micropores are more active in the toluene hydrogenation and the HDS of the dibenzothiophene than MoS_2 slabs.[11c,d] In addition, the argon sorption results show that the micropore-size distribution and micropore volume decrease with increased metal loadings in NB-MOR (Figure S7). This phenomenon might be related to the existence of the very small metal sulfide clusters in the micropores of NB-MOR.

Figure 3 shows catalytic data in the HDS of 4,6-DMDBT over activated CoMo/NB-MOR and CoMo/γ-Al_2O_3 catalysts. The reaction network of the HDS of the 4,6-DMDBT is shown in Figure S8. Compared with CoMo/γ-Al_2O_3 (61.5%), the CoMo/NB-MOR catalyst exhibits very high 4,6-DMDBT conversion (99.1%) (Figure 3a). Correspondingly, the lowest remaining sulfur content in the reaction products over CoMo/NB-MOR is 12 ppm, while that over the CoMo/γ-Al_2O_3 catalyst is 331 ppm (Figure 3b). These results indicate that the CoMo/NB-MOR catalyst shows an unprecedented high HDS activity. Very importantly, the CoMo/NB-MOR catalyst shows a long catalyst life. There is no activity loss for the CoMo/NB-MOR catalyst in the HDS of 4,6-DMDBT (Figure 3c). The good catalyst life of the CoMo/NB-MOR catalyst is one of the key features in applications of industrial catalysts. Additionally, the yield of the hydrocracking products (C_5-C_9) over the CoMo/NB-MOR catalyst (0.10%) is very low (Table S4), which is also an important factor for industrial applications of HDS catalysts.

It is worth mentioning that not only the CoMo/NB-MOR but also the NiMo/NB-MOR catalyst has excellent HDS activity (Figure S9). Moreover, we also tested the HDS activity of CoMo/NB-MOR for treating industrial diesel with a sulfur content of 5240 ppm. After reacting for 10 h, the remaining sulfur content in the product was below 20 ppm over the CoMo/NB-MOR catalyst, which is much lower than the value of about 500 ppm obtained over the CoMo/γ-Al_2O_3 catalyst (Figure S10). These results show the potential importance of industrial applications of the CoMo/NB-MOR catalyst in the future.

Because of the large size of the 4,6-DMDBT molecule, HDS mainly occurs in the mesopores rather than in the micropores over the CoMo/NB-MOR catalyst. Notably, although γ-Al_2O_3 has a larger mesopore surface area (288 m^2/g) than NB-MOR (182 m^2/g), the CoMo/NB-MOR catalyst exhibits much higher activity than the CoMo/γ-Al_2O_3 catalyst (the two catalysts have the same metal loading). This phenomenon is attributed to the difference in microporosity between the NB-MOR and γ-Al_2O_3 supports. The NB-MOR has a mesopore volume of 0.37 cm^3/g as well as a micropore volume of 0.13 cm^3/g, while the γ-Al_2O_3 only has a mesopore volume of 0.45 cm^3/g (Table S2). Possibly, the small molybdenum sulfide clusters in the micropores of the NB-MOR support create a large amount of spillover hydrogen, which then migrates onto nearby active CoMo sites in the mesopores; this can enhance the hydrogenating ability of the CoMo/NB-MOR catalyst. This suggestion is strongly supported by catalytic tests over the mesopore-free MOR-supported CoMo catalyst (CoMo/MOR) and the mechanical mixture of CoMo/NB-MOR or CoMo/γ-Al_2O_3 with CoMo/MOR (Figure 4). When mesopore-free MOR support is used, the CoMo/MOR catalyst shows very low conversion (1.7%) because the HDS of the bulky 4,6-DMDBT molecule only occurs on the external surface of the CoMo/MOR catalyst (Figure 4a). However, when the CoMo/NB-MOR catalyst is mechanically mixed with CoMo/MOR, the conversion reaches 82.1%. In contrast, CoMo/NB-MOR itself shows a conversion at 70.6% (Figure 4a). Interestingly, when pure MOR zeolite is added to CoMo/NB-MOR, the catalyst activity is close to CoMo/NB-MOR itself (Figure 4b). These results indicate that the very small metal sulfide clusters in the micropores play an important role in enhancing the HDS activities of the CoMo/NB-MOR catalyst. As expected, the 4,6-DMDBT conversion is also improved after mixing CoMo/γ-Al_2O_3 with the CoMo/MOR catalyst, increasing from 36.8% to 44.6% (Figure 4c). Furthermore, the selectivities for the hydrogenation products confirm that the hydrogenating ability of both CoMo/NB-MOR and CoMo/γ-Al_2O_3 catalysts is remarkably increased by mixing with CoMo/MOR (Table S5). Moreover, temperature-programmed desorption of ammonia (NH_3-TPD) curves showed that the acidity of the CoMo/NB-MOR catalyst is higher than that of the CoMo/γ-Al_2O_3 catalyst (Figure S11). So, the CoMo/NB-MOR catalyst exhibits higher selectivities for toluene and methylcyclohexane than the CoMo/γ-Al_2O_3 catalyst (Table S5) due to the cracking of 3,3′-dimethylcyclohexylbenzene.

In summary, we demonstrate a facile method for synthesizing novel zeolite nanofiber bundles containing parallel-mesopore channels. More importantly, CoMo and NiMo catalysts supported on these nanofiber bundles showed an unprecedented high activity and excellent catalyst life in the HDS of the 4,6-DMDBT and industrial diesel, compared with a conventional γ-alumina-supported CoMo catalyst. These features should be important in the future for design and preparation of multi-functional high activity catalysts for HDS, selective cracking, and hydrocracking.

ASSOCIATED CONTENT

Supporting Information

Experimental details, catalyst test, characterization, and the product selectivity of the HDS. This material is available free of charge via the Internet at http://pubs.acs.org.

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