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Highly active CoMo/Al (10) KIT-6 catalysts for HDS of DBT: Role of structure and aluminum heteroatom in the support matrix

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ABSTRACT

Herein we report the synthesis of CoMo catalysts for the hydrodesulfurization of dibenzothiophene reaction as a function of morphological effect and heteroatom substitution on KIT-6 supports. The interconnected pores of KIT-6 seem to play a vital role in the active catalyst preparation. The activity and direct desulfurization selectivity trends of the different catalysts resulted as follows: CoMo/Al(10)-KIT-6 > CoMo/KIT-6 > CoMo/ γ -Al₂O₃. The improved catalytic activity and direct desulfurization selectivity are attributed to: (I) the high surface area and interconnected pores of KIT-6 which allow large quantities of nanosized (< 4 nm) active CoMoS species and (II) the aluminum deposition on the surface of KIT-6 that creates mild acidity on the support, facilitating the dispersion of these nano-sized CoMoS species. Finally, evidence of the Al incorporation into the silica Matrix is presented.

Introduction

Environmental regulations are limiting the sulfur content in fuels to low levels (< 10 ppm) for a better quality of life for all living things [1]. Hydrodesulfurization (HDS) is the most common process to reduce the sulfur level from petroleum distillates. Nevertheless, it is hard to reach the sulfur limits from the heavier crudes with the current catalysts and processes. To elucidate this issue, many attempts have been taken at various levels. Among them, the preparation of better-supported hydrotreating catalyst is an important topic of research [2,3]. Different supports like alumina [4,5] silica [6,7] metal oxides [8], mixed metal oxides [9] and carbon [10], have been tested for hydrotreating reactions. After the invention of mesoporous silica sieves, a variety of these materials like MCM-41 [11,12], HMS [13,14], SBA-15 [15,16] and KIT-6 [17-19] have been used as a support of catalysts for the hydrotreating reactions. The general observation from these mesoporous supported hydrotreating catalyst is the vast surface area leading to substantial activity improvements. The nature and dimension of the pores also play a significant role for the improved activity. The heteroatom introduction on the surface of pure silica matrix extensively enhances the activity of the catalyst. The deposition of aluminum, titanium, and zirconium results in a positive improvement in the activity of hydrotreating reactions [20].

Among the different mesoporous supports, only a few studies were

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done on the unique 3D-KIT-6 materials. Soni et al. [17] studied the hydrotreating reaction using KIT-6 supported CoMo and NiMo catalysts finding a better dispersion of the active species and a faster diffusion of reactants and products on the KIT-6 supported catalysts. In this regard, the heteroatom effect in the KIT-6 was not yet tested as a support for HDS of the DBT reaction. Therefore, the present study is focused on the preparation of KIT-6 with and without aluminum and a fixed silica to aluminum ratio was used i.e. Si/Al = 10. The resultant material was used as a support of CoMo catalysts for the HDS of DBT; a set of catalyst via CoMo/KIT-6 and CoMo/Al (10)-KIT-6 was prepared and tested towards the HDS of DBT. The activity of all the catalysts was correlated with the physicochemical properties of the support and catalysts. Finally, the activities of the synthesized CoMo/KIT-6 catalysts were compared with a catalyst prepared using a commercial γ -Al₂O₃ support.

2. Materials and methods

2.1. Synthesis of KIT-6 support and CoMo catalysts

The KIT-6 material was synthesized using the procedure reported elsewhere [21]. To prepare aluminum incorporated KIT-6 (Si/Al = 10), the parent KIT-6 was stirred for 24 h at room temperature with a solution of aluminum isopropoxide in isopropanol. The solid products were filtered and washed with isopropanol, dried and calcined at 500 °C

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for 8 h [22]; these supports are represented as Al(10)KIT-6. All CoMo catalysts were prepared by simultaneous wet impregnation method using appropriate concentrations (5 wt.% Co and 14 wt.% Mo) of acetate salts. After the impregnation, the catalysts were dried at 100 °C for 12 h and calcined at 500 °C for 4 h.

2.2. Characterization

The low and high angle X-ray diffraction patterns were recorded with a Philips X'Pert Diffractometer using the Cu Ka radiation $(\lambda = 1.5418 \text{ Å})$, a nickel filter and a x'celerator as a detector. By using the real-time multiple strip detection technique, XRD patterns were collected in the 2θ range of 0.5–80. Surface areas of the supports and CoMo impregnated catalysts were analyzed by Micrometrics-Tristar II. Before the analysis, all the samples were degassed at 300 °C for 5 h under a vacuum atmosphere. The analysis was performed at liquid nitrogen temperature (77 K); the surface area was calculated from the BET plot, whereas the pore size distribution was measured by the BJH method. The coordination environments of Co and Mo in oxide catalysts were analyzed by a Varian CARY-300 UV-vis DRS spectrophotometer with a resolution of 0.24 nm. Solid state ²⁷Al MAS NMR spectra was recorded using BRUKER Switzerland, model Avance 400 MHz, spectrometer. The dried powdered samples were loaded into a BL4 X/Y/1H 4mm multinuclear probe and spun at 5 kHz according to the following protocol: Đ/2 pulse, 7 ís; CP contact time 2 ms; 1700 scans. An internal reference of the spectrometer was employed to calculate the chemical shifts. High-resolution transmission electron microscopy studies were performed using a JEOL JEM 2010 microscope (power 200 K eV). The solids were ultrasonically dispersed in alcohol, and the suspension was collected on carbon coated grids.

2.3. Hydrodesulfurization studies

The catalytic activity was evaluated in the hydrodesulfurization reaction of dibenzothiophene in a batch Parr reactor with a stirring rate of 700 rpm, T = 320 °C and a total hydrogen pressure of 55 bar. Prior to the reaction, the catalyst was sulfided ex-situ with an H2/H2S gas mixture (15 vol% H₂S, flow rate 60 mL min⁻¹) from 150 °C up to 400 °C (heating rate of 4 °C) and kept at this temperature for 2 h. After purging with the inert gas to eliminate the excess of H₂S, the sample was transferred to the reactor under Ar atmosphere. The reactor was charged with 0.2 g of sulfided catalyst (particle size between 80 and 100 mesh) and 100 mL of the feed composition, DBT (500 ppm of S) dissolved in 100 mL of n-hexadecane. Every reaction product was analyzed by GC in an Agilent 7890 instrument, using an Agilent 30 m HP-5 capillary column. The initial reaction rate was obtained from the plot of Ca⁰⁰ (500 ppm S) versus time and normalized by the reaction volume, and the sulfided catalyst mass used. Catalytic activity was expressed by the initial reaction rate (mol DBT transformed per second and gram of catalyst) [9].

3. Results and discussion

3.1. Characterization of supports and catalysts

The textural properties of supports and catalysts were studied by N₂ adsorption–desorption analysis. The textural analysis of γ -Al₂O₃ support showed an H4 hysteresis loop with a small slope in the capillary condensation regime, indicating a broad pore size distribution (Fig. 1A–a) [23] The general profile of the adsorption–desorption isotherm for the CoMo/ γ -Al₂O₃ catalyst resulted quite similar to that obtained for the γ -Al₂O₃ support. This suggests that the alumina textural properties resulted barely affected by the incorporation of the metals and the subsequent thermal treatment. The isotherms of KIT-6 (Fig. 1A–b) and Al (10) KIT-6 (Fig. 1A–c) display a typical type IV isotherm with two sharp inflections in the relative pressure range of

0.6–0.8 and an H1-type hysteresis loop confirming the orderly nature of the mesoporous KIT-6 (Fig. 1A). As expected the capillary condensation between the two inflections indicates the presence of uniform mesoporous channels [24]. After the introduction of aluminum and impregnation of the active metal compounds, the type-IV isotherm with H1-type hysteresis loop and narrow pore size distribution are still observed (Fig. 1B). The value corresponding to the surface area, pore volume and pore size of KIT-6, Al (10) KIT-6 and the corresponding CoMo catalyst is given in Table 1. A significant decrease in surface area and pore volume of supported CoMo catalysts was observed (Table 1). From the N₂ adsorption-desorption studies, it is concluded that the original structure of γ -Al₂O₃ and KIT-6 supports remains after the Al heteroatom deposition and active metals loadings as well.

The mesoporous nature of pure KIT-6, Al (10) KIT-6 supports (Fig. 2A (a, b)) and CoMo impregnated catalyst were confirmed by low angle X-ray diffraction analysis (Fig. 2A (c, d)). The low angle XRD patterns of calcined supports showed an intense peak at $2\theta = 0.9$ corresponding to the (211) plane, the hump about 1.1° is assigned to (220) planes and the two small peaks in the 2θ range of 1.5–2 related to (420) and (332) diffraction planes. These planes are characteristic of the three-dimensional mesoporous KIT-6 material (Fig. A-b) [22]. Even though a decrease in the peak intensity, the existence of all the XRD peaks at the characteristics 20 degrees confirms the mesoporous nature of the base material. For Co-Mo catalysts, the mesoporous nature of KIT-6 is retained even after the addition of almost 20 wt.% of metals (5% wt.% Co and 14 wt.% of Mo). The wide-angle XRD analysis gave information about the formation of different phases of Co and Mo oxides on γ -Al₂O₃, KIT-6, and Al (10) KIT-6, which are shown in the 20 range of 5-80 (Fig. 2B). The CoMo catalyst prepared using pure KIT-6 support showed weak peaks around $2\Theta = 23.2$ and 26.4 which possibly correspond to CoMo oxides of β-CoMoO₄ phase (JCPDS-21-0868). However, such short range peaks do not appear in the case of γ -Al₂O₃ and Al (10) KIT-6 supported catalyst. The absence of those peaks might indicate that the oxide precursors of the sulfide phase are well dispersed over the supports.

To clarify the nature of the Al in the KIT-6 matrix ²⁷Al NMR measurements help us to elucidated the coordination sphere of Al¹³⁺ ions. The obtained spectra for the γ -Al₂O₃ and Al(10) KIT-6 are showed in Fig. 3. The spectrum corresponding to γ -Al₂O₃ revealed the multiple Al environments, including the octahedral Al(6) centered at 4.9 ppm, the pentahedral Al(5) centered at 43.5 ppm, and the tetrahedral Al(4) centered at 65 ppm. As expected, the relative proportions of Al(4), Al(5) and Al(6) obtained by integration of the spectra confirm that in the γ - Al_2O_3 around 5.6% of the Al^{3+} ions are in tetrahedral coordination while 14.2% and 80.2% resulted in pentahedral and octahedral coordination respectively. These peaks are commonly obtained for disordered γ -Al₂O₃ phase [25,26]. For the spectrum correspondent to the Al(10)KIT-6, only two environments for the Al³⁺ ions were detected. In this case, the octahedral Al(6) was observed at -1.7 ppm and that signal related to tetrahedral Al(4) species was observed at 52.7 ppm. As seen, the relative quantities resulted very differently, almost showing an inverse behavior to that seen in the y-Al₂O₃ spectrum. Only 18.8% of the Al³⁺ ions were detected in octahedral coordination, while 81.2% resulted in tetrahedral coordination. This variation in the Al³⁺ ions coordination observed for the Al (10)KIT-6 material indicated that the aluminum is preferable as a part of the tetrahedral silica matrix and not as isolated or segregated Al₂O₃ over the surface of the KIT-6. Also, the formation of -Si-O-Al and O-Al-OH surface chemical environment can lead to the shift observed to lower ppm values of the ²⁷Al signal. These results are in line with the reduced intensity observed in the XRD Al(10)KIT-6 pattern; both effects confirm the incorporation of aluminum into the silica matrix.

High-resolution TEM is a valuable and informative technique to identify the morphology of the catalytically active phase via monitoring the MoS_2 slabs on the support matrix [27]. Fig. 4 shows selected HRTEM micrographs for the different CoMo sulfided catalysts. In all of

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Fig. 1. Adsorption-desorption isotherms (A, B) and pore size distribution (C, D) of a) Al₂O₃, b) KIT-6, C) Al (10) KIT-6 supports and d) Al₂O₃, e) KIT-6, f) Al (10) KIT-6 CoMo catalysts.

 Table 1

 Textural properties for calcined supports and CoMo catalysts.

Sample	$S_{BET} (m^2 g^{-1})$	Vp (cm ³ g ⁻¹)	Dp (nm)
γ -Al ₂ O ₃	226	0.62	8.5
KIT-6	818	0.88	4.9
Al(10)KIT-6	627	0.70	5.0
CoMo/y-Al ₂ O ₃	177	0.46	8.0
CoMo/KIT-6	502	0.60	5.1
CoMo/Al(10)KIT-6	323	0.45	5.3



Fig. 2. Low (A) and high angle (B) XRD patterns for supports and CoMo catalysts. In A: a) KIT-6 b) Al (10) KIT-6, c) CoMo/KIT-6, d) CoMo/Al (10) KIT-6. In B CoMo catalysts supported on a) γ -Al₂O₃, b) KIT-6, and c) Al (10) KIT-6.

them, a large quantity of MoS₂ was observed varying the particle size and stacking nature. To make quantitative comparisons, the length and layer number of MoS₂ slabs were measured by statistical analysis (Fig. 5). For this analysis, about 25 micrographs including a minimum of 200 slabs were taken from different parts of each catalyst. The catalyst prepared using Al (10) KIT-6 support displayed MoS₂ predominantly in the form of two stacked slabs with a small particle size $(\sim 2 \text{ nm})$ in comparison with KIT-6 and commercial γ -Al₂O₃ supported CoMo catalyst. The commercial y-Al₂O₃ and KIT-6 supported CoMo catalyst forms about the 3-4 stacking of MoS2, and the length of the former is longer than the later. The size and stacking number of the MoS₂ are expected to reflect in the activity results of the catalysts. The average slab length for the samples resulted in 4.5, 4.1 and 3.6 nm for CoMo/y-Al2O3, CoMo/KIT-6 and CoMo/Al(10)KIT-6 catalysts respectively. In the case of the average stacking number of the MoS₂ resulted as follows, 3.88, 3.75 and 3.21 slabs for CoMo/y-Al2O3, CoMo/KIT-6



Fig. 3. ²⁷Al NMR spectra for commercial γ -Al₂O₃ and Al(10)-KIT-6 samples.

and CoMo/Al(10)KIT-6 catalysts respectively. These analyses are in agreement with observations previously reported with similar materials [28].

UV-vis diffuse reflectance spectroscopy was used to determine the symmetry of Co and Mo species in the CoMo samples. The corresponding electronic spectra of the calcined CoMo/KIT-6, CoMo/Al (10) KIT-6, and CoMo/y-Al2O3 oxide catalyst are shown in Fig. 6. The band appearing around 220-270 and 300-330 nm are assigned to charge transfer transitions in isolated tetrahedral MoO₄²⁻ and octahedral Mo⁶⁺ species, respectively [29]. In all three catalysts, a small hump appears around 400 nm and can be attributed to octahedral Co²⁺ species [30]. T. A. Zepeda et al. [14] discussed in detail about the various possible energy level spectra of CoMo catalyst on pure silica, and Ti modified HMS supports. From these studies, the bands appearing at 400 and 700 nm can be attributed to Co^{2+} and Co^{3+} while the broadband appearing around 650 nm might be assigned to the presence of tetrahedral Co²⁺ species [31]. However, as our XRD results indicated, the possible presence of the CoMoO₄ was pointed out, this inverse spinel could lead to the formation of octahedral Co complexes



Fig. 4. Selected HRTEM micrographs for A) CoMo/γ-Al₂O₃, B) CoMo/KIT-6 and C) CoMo/Al (10) KIT-6 catalysts.



Fig. 5. Statistical analysis of the HRTEM micrographs for the a) $CoMo/\gamma$ -Al₂O₃, b) CoMo/KIT-6 and c) CoMo/Al (10) KIT-6 catalysts, A) stacking number B) slab length.



Fig. 6. DR-UV Vis spectroscopy study for a) CoMo/ γ -Al₂O₃, b) CoMo/KIT-6 and c) CoMo/Al (10) KIT-6 catalysts.

associated with d–d transitions, and therefore the broadband at 650 nm could be rather assigned to Co^{2+} ions occupying octahedral sites [30]. The shift of peaks towards a higher wavelength region (indicated by an arrow) of the catalysts varied significantly even with the same quantity of active metals. This implies that the support matrix impacts the dispersion and formation of different domain sizes of the active catalytic species. DRS-UV spectra imply that the shift of bands towards a higher wavelength region (marked with an arrow) indicates a formation of a large domain size of the active species.

3.2. Hydrodesulfurization activity

The activity for the ex-situ sulfided catalysts was evaluated in the HDS reaction of DBT in a batch reactor at 320 °C under a total hydrogen pressure of 55 bar. Fig. 7. A represents the conversion of the different

catalysts as a function of time. The conversion profile follows the same behavior indicating the same reaction kinetic order for all catalysts tested. However, a significant variation was observed within the three catalysts since the loading mass of each material in their respective reaction was strictly the same. Taking the former into account and when comparing only the conversion at 180 min of reaction time, the catalyst prepared using commercial γ -Al₂O₃ as support has 40% conversion. The KIT-6 supported catalyst showed 75% and the Al (10) KIT-6 supported catalyst displayed around 95% conversion. The Al (10) KIT-6 supported CoMo catalyst completely converted all the DBT molecule at a period of 240 min.

Regardless the support, the reaction products observed were biphenyl (main product), tetrahydrodibenzothiophene (traces), cyclohexyl benzene (CHB) and dicyclohexyl (DCH). Many literature reports explain the possible HDS reaction mechanism of DBT; it occurs through two main pathways: hydrogenation (HYD) and direct desulfurization (DDS) [32]. Fig. 7B shows the selectivity achieved at 30% DBT conversion for the three catalysts. The γ -Al₂O₃ supported CoMo catalyst demonstrated a selectivity of 50% throughout the DDS pathway, while the value of DDS selectivity increased to about 80% and 90% for the KIT-6 supported catalyst and Al (10) KIT-6 supported catalyst respectively. So the trend in the DDS route of the catalyst resulted in the following order: CoMo/Al (10) KIT-6 > CoMo/KIT-6 > CoMo/ γ -Al₂O₃. The preferential formation of biphenyl in KIT-6 and Al (10) KIT-6 supported CoMo catalysts indicates that the DDS route was more favorable than the HYD route.

The initial reaction rates as a function of different catalyst are shown in Fig. 7C and two important points appear: (I) CoMo/KIT-6 catalyst show a higher activity than the commercial γ -Al₂O₃ supported catalyst, and (II) the activity of the CoMo-KIT 6 catalyst was increased due to the aluminum heteroatom deposition. The relative order of catalytic activity was: CoMo/Al (10) KIT-6 > CoMo/KIT-6 > CoMo/ γ -Al₂O₃. This is similar to the DDS selectivity trend indicating that more active sites responsible for DDS reaction were created on CoMo/KIT-6 and CoMo/Al (10) KIT-6.

4. Conclusions

In this work, CoMo HDS catalysts were prepared as a function of the support and aluminum heteroatom deposition in the support matrix. The CoMo catalyst prepared on KIT-6 support showed higher activity than the commercial γ -Al₂O₃ supported catalyst, whereas the highest activity was observed for the catalyst prepared using the Al (10) KIT-6 as a support. The improved activity was explained in the following way: (I) The high surface area and interconnected pore nature of KIT-6 support may allow large quantities of active Co and Mo species in a fine dispersion, forming nanosized (< 4 nm) active MoS₂ species. (II) The aluminum deposition on KIT-6 creates mild acidity on the support, which facilitates the formation of nanosized MoS₂. Therefore, this study concludes that Al(10)KIT-6 support is a suitable material for supported CoMo hydrodesulfurization catalysts with high selectivity for the DDS pathway.



Fig. 7. Catalytic activity results for the HDS of DBT A) DBT conversion, B) % selectivity, C) Initial reaction rate for a) CoMo/Y-Al₂O₃, b) CoMo/KIT-6 and c) CoMo/Al (10) KIT-6. Catalytic test conditions: 500 ppm of S from DBT, 320 °C, 800 psi of H₂ and 700 RPM.

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