Effect of Al-SBA-15 support on catalytic functionalities of hydrotreating catalysts

I. Effect of variation of Si/Al ratio on catalytic functionalities

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Abstract

SBA-15 and Al-SBA-15 of varying Si/Al ratios (10–40) were synthesized by well-known procedures. Characterization using XRD, pore size distribution, 27Al NMR confirmed that hexagonal mesoporous structure is obtained and majority of Al is in tetrahedral positions. Mo, CoMo and NiMo catalysts prepared using these supports were examined by XRD, oxygen uptakes in sulfided state and temperature programmed reduction (TPR). The catalysts were tested for hydrodesulfurization (HDS) of thiophene and hydrogenation of cyclohexene. Systematic variation of oxygen chemisorption and catalytic activities were observed as a function of Si/Al ratio. The systematic variation of activities, oxygen chemisorption and TPR hydrogen consumption of Mo indicated that the molybdenum dispersion and anion vacancies, and catalytic activities are significantly influenced by support Al content. Compared to SBA-15, Al-SBA-15 supported Mo, CoMo and NiMo catalysts show outstanding activities for hydrogenation.

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1. Introduction

Environmental restrictions on petroleum products to limit the sulfur level in fuels to 50 ppm or lower necessitated new generation hydrodesulfurization catalysts. In addition, preparing hydrocarbon fuel feeds to the fuel cell set up requires sulfur reduction to 0.1 ppm. Such a demanding task requires catalysts that are seven times more active than the present catalysts used to achieve 500 ppm sulfur [1]. It is not only the high activity but they should also have different activity profiles with respect to different functionalities. In order to modify the activity to achieve the above said objectives several approaches have been pursued among which variation of support is an important one [2].

γ-Al2O3 is the only support used in commercial HDS catalysts. Many other supports like SiO2 [3], carbon [4], oxides [5–7] and mixed oxides [8] have been studied. In recent times, the attention is shifted to zeolites like Y, USY and mesoporous materials like MCM-41 [9,10], HMS [11,12], SBA-15 [13] and mesoporous Al2O3 [14] systems. MCM-41 supported CoMo catalysts are reported to exhibit higher activities for conversion of benzo thiophene and petroleum residues. Song and Reddy [15] demonstrated that CoMo/MCM-41 is substantially more active than CoMo/γ-Al2O3 catalysts at high molybdenum loadings. Chiranjeevi et al. [16] reported that Al-HMS materials based CoMo, NiW catalysts showed superior activities compared to γ-Al2O3 supported catalysts. Highly active MoS2 catalysts supported on mesoporous Al2O3 were reported by Zdrazil and co-workers [14]. Vradman et al. [17] reported higher activities for HDS and hydrogenation using Ni-W/SBA-15 catalysts. Results reported by Klimova et al. [18] on Al-SBA-16 supported NiMo catalysts for HDS of 4,6-DMDBT hydrodesulfurization indicated that these materials exhibited high activities in conversion of the above said refractory sulfur compound. Zepeda et al. [19] reported on Ti-HMS of various Si/Ti ratios for HDS of benzo thiophene suggested that Ti containing HMS supported catalysts

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displayed higher activities than the γ-Al2O3 supported catalysts. Chiranjeevi et al. reported systematic relationships for HDS and HYD activities as a function of Si/Al ratio of Al-HMS supported Mo catalysts [20]. In this investigation we are reporting a detailed systematic study on Mo, CoMo and NiMo supported on Al-SBA-15 of various Si/Al ratios for HDS and HYD functionalities.

2. Experimental

2.1. Synthesis

The SBA-15 and Al-SBA-15 materials were synthesized by following published procedure [21,22]. The incorporation of Al into SBA-15 mesostructure was carried out by direct synthesis method using Al-isopropoxide as Al source following published procedure [22]. In a typical synthesis, 9 ml tetra ethyl ortho silicate (TEOS) and a calculated amount of aluminum isopropoxide in order to obtain a Si/Al ratio equal to 10, 20, 30 and 40 are added to 10 ml of aqueous HCl solution at pH 1.5. This solution is stirred for over 3 h and then added to a second solution containing 4 g triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) copolymer (EO20:PO70:EO20) in 150 ml of HCl aqueous solution at pH 1.5 at 40 °C. The mixture is stirred for 1 h at the same temperature and allowed to react at 100 °C for 48 h. The solid product obtained was filtered off, dried at 110 °C overnight and calcined at 550 °C for 6 h. The sample is designated as Al-SBA-15 (X), where X stands for the Si/Al ratio.

The molybdenum and promoted catalysts (Co or Ni) were prepared by successive incipient wetness impregnation method by taking appropriate concentrations of ammonium hepta molybdate and corresponding nitrate salts of the promoters in order to obtain 8 wt% Mo and 3 wt% Co (or Ni) using Al-SBA-15 supports of varying Si/Al ratios. All the catalysts were dried in oven at 110 °C overnight and calcined at 550 °C for 6 h.

2.2. Characterization

The calcined mesoporous Al-SBA-15 (X) supports were characterized by low angle XRD, nitrogen adsorption–desorption analysis and 27Al MAS NMR. All the catalysts were characterized by XRD, BET surface area, temperature programmed reduction (TPR) and low temperature oxygen chemisorption (LTOC). Temperature programmed reduction profiles of catalysts were obtained using TPD/TPR-2900 Micromeritics (USA) instrument for analyzing the nature of reducible metal species present on the support. TPR profiles were taken from ambient temperature to 1000 °C (10 °C/min) and then the temperature was kept isothermal for 30 min. A 5% H2/Ar mixture at a flow rate of 50 ml/min was used as reducing gas. The hydrogen consumption corresponding to the reduction of metal oxide at various stages of reduction were computed from the peak area calibrated with a standard Ag2O. The H2 consumption per Mo is calculated by dividing total hydrogen consumption per gram of catalyst by metal content. The low temperature oxygen chemisorption was measured at −78 °C in a conventional high vacuum system, on a catalyst sulfided at 400 °C for 2 h using CS2/H2 mixture at a flow rate of 40 ml/min, according to double isotherm procedure reported by Parekh and Weller [23] for reduced catalysts. The same system was used for the BET surface area measurements.

2.3. Catalytic activities

The hydrodesulfurization (HDS) of thiophene and hydrogenation (HYD) of cyclohexene were carried out at 400 °C on a catalyst sulfided at the same temperature for 2 h in a flow of CS2/H2 mixture, in a fixed-bed reactor operating at atmospheric pressure and interfaced with on-line gas chromatograph equipped with six-way sampling valve for product analysis [24]. The first-order rates were evaluated according the equation \[ x = \frac{r(W/F)}{x} \] where \( r \) is the rate in moles per hour per gram, \( x \) the fractional conversion, \( W \) the weight of the catalyst in grams and \( F \) is the flow rate of the reactant in moles per hour [7,24]. The rates thus calculated for HDS and HYD reactions are taken as a measure of HDS or HYD activity. The conversions were kept (below 15%) to avoid diffusion limitations.

3. Results and discussion

3.1. Synthesis and characterization of the support

Al-SBA-15 materials with varying Si/Al ratios were characterized by XRD, BET surface area, pore size and 27Al NMR methods. The results indicated the hexagonal mesoporous structure is obtained as supported by low angle XRD peak (Fig. 1) and narrow pore size distribution centered around 78 Å. 27Al NMR results indicated that majority of Al is in tetrahedral
surroundings \[25,26\]. It was inferred from the results that the high surface area hexagonal mesoporous Al-SBA-15 is obtained at all Si/Al ratios. Detailed support characterization is given elsewhere \[28\].

### 3.2. Characterization of Mo, CoMo and NiMo catalysts

The BET surface area of Mo, CoMo and NiMo catalysts as a function of Si/Al ratio of Al-SBA-15 support are shown in Table 1. It can be seen that the surface area in all these cases decreases in a linear manner with the increase of Si/Al ratio of the support. Mo, CoMo and NiMo catalysts exhibited similar surface areas at each Si/Al ratio indicating that there is no significant change in surface area with the addition of promoters. A comparison of Al-SBA-15 (10), 8%Mo/Al-SBA-15 (10) and 3%Co8%Mo/Al-SBA-15 (10) with respect to pore size distribution is presented in Fig. 2. It can be seen that a narrow pore size distribution is retained in the molybdenum supported catalyst indicating that Al-SBA-15 (10) pore structure is intact after molybdenum addition. However, the pore volume slightly decreased and the mean pore diameter is shifted marginally towards higher values suggested that minor changes occurred with introduction of Mo on Al-SBA-15 (10). A comparison of 8%Mo/Al-SBA-15 (10) and 3%Co8%Mo/Al-SBA-15 (10) reveals that the pore size distribution did not change appreciably suggesting that structural integrity is retained after addition of cobalt also.

Mo, CoMo and NiMo supported on SBA-15 and Al-SBA-15 were examined by XRD. These studies indicated that there is a broad hump due to amorphous silica between 15 and 40 \(2\theta\) values for the pure Al-SBA-15 (10) support. The Mo/Al-SBA-15 (10) also exhibited similar pattern, there is no evidence in the XRD pattern for crystalline MoO\(_3\) indicating that MoO\(_3\) is well dispersed in this catalyst. The XRD pattern of CoMo catalysts supported on Al-SBA-15 supports is very similar to Mo/Al-SBA-15 (10) except that there is a small broad peak superimposed on the amorphous silica hump. This peak positioned at \(2\theta\) 26.3, may be attributed to the highly dispersed CoMoO\(_4\). The broadness of the peak indicated that the CoMoO\(_4\) phase is of small crystallite size. Similar results are observed on NiMo catalysts with various Si/Al ratios of Al-SBA-15 supports. However, there is no evidence for the presence of NiMoO\(_4\), if at all NiMoO\(_4\) is present it is in well-dispersed state with crystallite size below 40 Å. These results indicate that Mo, CoMo and NiMo is well dispersed on all the catalysts presented.

The Mo, CoMo and NiMo catalysts on various Si/Al ratio of SBA-15 supports were examined by temperature programmed reduction. Typical results and quantitative data on SBA-15 of various Si/Al ratios are shown in Fig. 3 and Table 2, respectively. The TPR pattern of pure support is also shown in Fig. 3. It can be noted that pure support does not show any

![Fig. 2. BJH pore size distribution of calcined Al-SBA-15, 8%Mo/Al-SBA-15 and 3%Co8%Mo/Al-SBA-15 samples at Si/Al ratio 10.](image)

![Fig. 3. TPR profiles of Al-SBA-15 (10) supported Mo, CoMo and NiMo catalysts.](image)
reduction at all the temperatures studied. All the catalysts containing Mo, CoMo and NiMo show a sharp reduction feature followed by a broad feature at high temperature. It can be noticed that in the case of promoted catalysts the low temperature peak shifts to further lower temperatures. The shift is more in the case of Ni promoted catalyst. It appears that the promoters help molybdenum to reduce at lower temperatures.

Hydrogen consumption per gram of Mo is calculated for molybdenum catalysts supported on Al-SBA-15 with varying Si/Al ratios and their relationship with activities will be discussed after discussing activity data.

Oxygen uptakes on Mo, CoMo and NiMo catalysts evaluated in sulfided state on catalysts supported on Al-SBA-15 of various Si/Al ratios are shown in Table 1 and Fig. 4a. It can be seen that oxygen uptakes decrease significantly with increase of Si/Al ratio. The oxygen uptakes decreased from 85.3 $\mu$mol/g for Si/Al ratio 10 to 27.2 $\mu$mol/g in the case of Si/Al ratio 40. However, it can be noted from Fig. 4a that the decrease is linear and systematic with Si/Al ratio and is similar for Mo, CoMo and NiMo catalysts. The difference between Mo and CoMo, NiMo catalysts is only marginal indicating that Co and Ni may not be contributing significantly to the oxygen chemisorption. It is well known that oxygen uptake represents number of anion vacancies and is also related to the dispersion of MoS₂ [27]. Therefore, it appears that number of anion vacancies is increasing with increase of Al content in the support. It can also be inferred that in Mo, CoMo and NiMo catalysts the molybdenum dispersion did not vary significantly. The decrease of oxygen uptakes and hence dispersion as a function of Si/Al ratio can be interpreted as due to variation of the availability of aluminum ions that bind molybdenum. Our results on cumene cracking activity as well as acidity also varied in similar manner as a function of Si/Al ratio also supports the conclusion [28].

3.3. Variation of catalytic activities as a function of Si/Al ratio of the support

The catalytic activities for hydrodesulfurization of thiophene and hydrogenation of cyclohexene were evaluated on sulfided catalysts at 400 °C are presented in Table 3. It can be noted that the rate of HDS and hydrogenation increase with Al content on Mo, CoMo and NiMo catalysts. The catalytic activity for HDS and hydrogenation more than doubled when Si/Al ratio is varied from 40 to 10. The variation in catalytic activities for HDS and HYD are shown in Fig. 4b and c. There is a linear and systematic decrease of catalytic activity with the increase of Si/Al ratio of the Al-SBA-15 support. It can also be noted that there is significant promotional effect by Co and Ni for both HDS and HYD reactions. However, the promotional effects of Co for HDS is better for molybdenum supported on

### Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>Reduction peak temperature (°C)</th>
<th>H₂ consumption per gram catalyst (ml)</th>
<th>H₂ consumption per gram Mo^b (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-SBA-15 (10)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>8%Mo/Al-SBA-15 (10)</td>
<td>563</td>
<td>45.4</td>
<td>567</td>
</tr>
<tr>
<td>8%Mo/Al-SBA-15 (20)</td>
<td>564</td>
<td>41.6</td>
<td>520</td>
</tr>
<tr>
<td>8%Mo/Al-SBA-15 (20)</td>
<td>559</td>
<td>37.5</td>
<td>469</td>
</tr>
<tr>
<td>8%Mo/Al-SBA-15 (40)</td>
<td>529</td>
<td>33.7</td>
<td>422</td>
</tr>
<tr>
<td>3%Co8%Mo/Al-SBA-15 (10)^c</td>
<td>532</td>
<td>45.5</td>
<td>568</td>
</tr>
<tr>
<td>3%Ni8%Mo/Al-SBA-15 (10)^c</td>
<td>475</td>
<td>42.5</td>
<td>531</td>
</tr>
</tbody>
</table>

^a H₂ consumption per gram of catalyst was calculated from the raw peak area calibrated with standard Ag₂O reduction.

^b H₂ consumption per gram of molybdenum was calculated from the corresponding data for catalyst divided with amount of molybdenum content.

^c H₂ consumption is less reliable due to contribution from reduction of promoter oxide.

Fig. 4. Effect of Si/Al ratio of Al-SBA-15 on oxygen uptake (a) and reaction rates (b and c) of Mo, CoMo and NiMo catalysts.
Al-SBA-15 at all Si/Al ratios. But in the case of hydrogenation Ni seems to be a better promoter. It is well known that Co is a better promoter for HDS and Ni is superior for hydrogenation on γ-Al2O3 supported catalysts [29,30]. It can be recalled that earlier we have noticed that oxygen chemisorption also varied in a similar manner as a function of Si/Al ratio. This relationship will be further discussed when discussing activity versus O2 uptake correlations.

The $k_{\text{HYD}}/k_{\text{HDS}}$ ratios as a function of Si/Al ratio of the support are presented in Table 3. It can be noted that on Mo catalysts the Si/Al ratio did not show any systematic variation but remained more or less constant. However, the ratio decreases with Al content in the support both in the case of Co and Ni promoted catalysts. It suggests that Al rich samples exhibit better hydrogenation abilities compared to silica rich catalysts. This observation will be discussed further while comparing SBA-15 and Al-SBA-15 supported catalysts in the forthcoming discussion.

### 3.4. Correlation of catalytic activity with oxygen uptakes

Correlation of oxygen uptakes with catalytic activity for HDS and HYD on Mo and NiMo catalysts are shown in Fig. 5. It can be seen that a linear correlation passing through origin is obtained both in the case of HDS and HYD for Mo as well as NiMo catalysts. Oxygen chemisorbs on anion vacancies and represents number of anion vacancies in Mo and W systems [27]. It is also well known that HDS and HYD reactions also take place on anion vacancies [31]. Therefore, it is not a surprise to see such a correlation. However, on amorphous silica–alumina supported Mo catalysts such nice correlations are not obtained as a function of SiO2–Al2O3 composition and also the correlation is not linear and different for HDS and hydrogenation [32]. We did not observe linear correlations with composition in any of the mixed oxide supports, such as SiO2–ZrO2, ZrO2–Al2O3, TiO2–Al2O3 and ZrO2–TiO2, etc., supported Mo systems [8]. Indeed, we observed such correlations in the case of Al-HMS and USY zeolite supported Mo, CoMo and NiMo catalysts as a function of Si/Al ratio [20,33]. It appears that the availability of well-defined uniform sites of Al in zeolite or zeolite like structures as a function of Si/Al ratio to anchor molybdenum is responsible for such systematic variation in catalytic properties. These uniform centers fix the molybdenum in highly dispersed state. In the promoted catalysts, the high dispersion of Mo provides greater number of edge sites to accommodate promoter atoms.

It is interesting to note that oxygen chemisorption correlates both with HDS and HYD indicating that oxygen chemisorption is not specific to any of the functionalities. This observation also leads to the conclusion that support indeed alters the properties of supported phase in a subtle way.

The temperature programmed reduction profiles on various molybdenum catalysts as a function of Si/Al ratio were evaluated as described in experimental sections. The results on promoted catalysts are presented in Fig. 3. From the TPR patterns hydrogen consumption per gram of Mo were evaluated for various Mo catalysts and plotted against reaction rates for HDS and HYD is shown in Fig. 6 and quantitative data are given in Table 2. It can be seen that both HDS and HYD rates vary in a linear manner with reducibility per gram of Mo. It can be noted that the reducibility of the supported Mo phase increases with the AI content in the support and catalytic activities also vary in a similar manner. It is interesting to recall that similar relationships are obtained in the case of oxygen chemisorption as a function of Si/Al ratio. It is well known that oxygen chemisorbs on anion vacancies and these anion...
vacancies are created under reducing conditions that are prevalent during sulfiding and reaction studies. Therefore, it appears change in reducibility is causing increase in anion vacancies at the edge sites as evidenced by increase of oxygen uptakes. This change in anion vacancies is responsible for the change in catalytic activities as function of Si/Al ratio of Al-SBA-15 supported Mo, CoMo and NiMo catalysts.

3.5. Comparison of Al-SBA-15 supported Mo, CoMo and NiMo catalysts with γ-Al2O3 and SBA-15 supported catalysts

A comparison of 8%Mo, 3%Co8%Mo and 3%Ni8%Mo on SBA-15, Al-SBA-15 and γ-Al2O3 supported catalysts for HDS and HYD are shown in Fig. 7. It can be noted that significant support effect can be noticed when compared to γ-Al2O3. Both SBA-15 and Al-SBA-15 (10) display superior activities for HDS and HYD compared to γ-Al2O3 supported catalysts. Al-SBA-15 (10) supported catalysts are 1.3–2.4 times more active for HDS and 2.4–3.1 times more active for HYD compared to γ-Al2O3 supported catalysts.

A comparison between SBA-15 and Al-SBA-15 reveals that Al-SBA-15 supported Mo, CoMo and NiMo catalysts are 0.9–1.5 times more active for HDS than SBA-15 supported catalysts. The comparison in the case of hydrogenation revealed that Al-SBA-15 supported catalysts are 1.3–2.4 times more active than SBA-15 supported counterparts. It is interesting to see that Al-SBA-15 (10) supported Mo, CoMo and NiMo catalysts increase HYD functionality significantly compared to SBA-15. It is important to note that HDS and HYD are promoted to different extent on different supports indicating that the support can independently vary the catalytic functionalities. The independent variation of the two functionalities also suggests that HDS and HYD may be originating from different set of sites.

4. Conclusions

The Mo, CoMo and NiMo catalysts were prepared by using high surface area Al-SBA-15 supports of varying Si/Al ratios. The surface areas of promoted catalysts are comparable to that of Mo catalysts. XRD examination of Mo, CoMo and NiMo catalysts indicated very high dispersion of Mo in unpromoted and promoted catalysts. The TPR results indicated that the promoters decreased the reduction temperature of molybdenum. The oxygen chemisorption on sulfided catalysts varied linearly with Si/Al ratio of the support. The results suggested that anion vacancy on molybdenum sulfide phase as well as its dispersion decreases with increase of Si/Al ratio.

The catalytic activities for HDS and HYD of Mo, CoMo and NiMo catalysts showed a linear systematic decrease with increase of Si/Al ratio of Al-SBA-15 support, similar to oxygen uptakes. A linear correlation passing through origin is obtained between catalytic activities and oxygen uptakes suggesting that the increase in anion vacancies is indeed responsible for the observed variation of HDS and HYD activities. HDS and HYD activities are varied linearly with reducibility per gram of Mo suggesting that the reducibility of the supported phase is influenced by the composition of the support.

A comparison of Al-SBA-15 with γ-Al2O3 and SBA-15 revealed that both SBA-15 and Al-SBA-15 supported catalysts display higher activities compared to γ-Al2O3 supported catalysts. SBA-15 and Al-SBA-15 supported catalysts showed similar activities for HDS but in the case of HYD, Al-SBA-15 is clearly superior to SBA-15 as a support for Mo, CoMo and NiMo catalysts. It appears high molybdenum dispersion on isolated Al sites in Al-SBA-15 and consequent increase of anion vacancies at the edge sites of Mo as a function of Si/Al ratio appears to be responsible for the outstanding activities of SBA-15 and Al-SBA-15 supported catalysts.

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