



Effect of hetero atom on dispersion of NiMo phase on M-SBA-15 (M = Zr, Ti, Ti-Zr)

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ABSTRACT

NiMo catalysts were prepared on different hetero atom doped SBA-15 supports for hydrotreatment evaluation. The nature of the hetero atom (Ti, Zr and TiZr) was observed to have a profound impact on the final molybdenum phase formed after calcination of the catalysts. Mo L₃ edge XANES analysis of the catalysts along with results from Raman and XRD, show that Zr-SBA-15 support is able to disperse the Molybdenum oxide phase better than the other supports. The formation of bulk phases viz., MoO₃ and NiMoO₄ is accelerated in pure SBA-15 supports. Evidence of Mo present as tetrahedral MoO₄ units was only found in TiZr-SBA-15 support. The presence of tetrahedral Mo species on TiZr-SBA-15 support was attributed to be due to the relative positive charge on the Zr site arising from the electronegative difference between Ti and Zr leading to [MoO₄]²⁻ stabilization. Sulfidation studies of the catalysts revealed that formation of active NiMoS phase is maximum in Zr-SBA-15 support and minimum in the SBA-15 supported catalysts. The low sulfidation of Mo in SBA-15 and TiZr-SBA-15 was due to the presence of bulk MoO₃ phase. The hydrotreating activities were in confirmation with the characterization studies, with NiMo/Zr-SBA-15 and NiMo/Ti-SBA-15 exhibiting highest HDS and HDN conversions respectively.

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1. Introduction

Development of highly active hydrotreating catalyst is necessary in order to meet increasing stringent environmental regulations and worldwide urge for eco-friendly and environmentally sustainable petroleum products. Current research in petroleum refining is focused on producing clean fuels with sulfur level below 15 ppm. However, its reduction to 15 ppm level is a challenging task. Theoretical studies have postulated that to bring sulfur level from 500 ppm to 15 ppm level, catalysts are required which are ~7 times more active than existing ones. γ -Alumina, which is widely used support in hydrotreating, has desirable properties including strong mechanical and textural properties, high dispersion for active transition metals and low cost [1]. However, one of the negative aspects of γ -alumina is the strong chemical interaction between the alumina and the transition metal catalysts in their oxide phase [2]. The quest to avoid the main disadvantage of alumina has led researchers to explore alternative superior support materials for hydrotreating reactions. Different materials have been assayed as new supports for hydrotreating catalysts, namely, silica [1,2], zirconia [3–5], titania [1,5,6], carbon [7], mixed oxides (ZrO₂–Al₂O₃ [8–10], ZrO₂–SiO₂ [10,11], ZrO₂–TiO₂ [12]), mesoporous materials like MCM-41 [13–17], SBA-15 [17,18] etc. Several

reviews are available for detailed analysis of the support effect on hydrotreating activity [19,20].

The catalytic properties of the molybdates are closely related to their structure. Silica has weak interaction with active metals and the detailed state of the deposited metal may still depend on a variety of parameters such as hetero atoms in silica material, its pretreatment and synthesis procedure etc. The effect of synthesis procedure on the formation of active phase was studied by Thielemann et al. [21]. At low Mo densities (≤ 0.8 Mo/nm²) the surface molybdenum oxide structures do not depend on the preparation procedure and the molybdenum oxide surface species at low loadings is found to be composed of both di- or oligomeric molybdenum oxide centres and isolated centres. The presence of tetrahedrally and octahedrally coordinated MoO₄ and MoO₆ centers was found on the surface of the SBA-15. It was also reported in the literature that dispersed molybdenum oxides on SBA-15 was present as monomeric and dimeric/oligomeric molybdenum oxide species at a density of 0.8–2.2 Mo/nm² [22–26]. Based on the EXAFS and Raman results, hexagonal MoO₃ like species were reported on SBA-15 at a molybdenum oxide concentration of 0.9 Mo/nm², besides traces of α -MoO₃ [27,28]. Isolated dioxo molybdenum oxide species were also reported at a density of 0.8 Mo/nm² [24]. Many papers are published in the literature to study the structure and interaction between different active components using chemisorptions technique [29–34].

Regarding silica-based molybdenum oxide systems, different results can be found in the literature using Raman, UV–vis and XAS

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analysis [35–42]. Among different supports and their combinations, TiO_2 and ZrO_2 have attracted attention due to the higher intrinsic hydrodesulphurization (HDS) activity demonstrated by Mo catalysts supported on these oxides in comparison with alumina-supported counterpart [3,6,9]. In addition, it was found that Ni-Mo catalyst supported on ZrO_2 has higher catalytic activity in HDS of thiophene than that supported on TiO_2 [5]. However, pure titania and zirconia supports in their oxide form possesses low surface area and porosity which is a disadvantage. Despite the high intrinsic activity (per Mo atom) of these supports, the specific activity (per gram of catalyst) remained lower than on alumina [5]. Furthermore, the study of MoO_3 dispersion on mixed oxides showed that interaction between Mo and Al is more compared to interaction between Mo and Ti or Zr based on XPS analysis [43]. Ti and Zr interacts equally with Mo and contributes equally to the dispersion. The study of the effect of hetero atoms on the structure and interaction of molybdenum oxide supported on SBA-15 is rather rare in literature. In this context, we investigate the structure of M-SBA-15 (M = Si, Ti, Zr and Ti-Zr) supported nickel-molybdenum oxides ($\text{Ni}_x\text{Mo}_y\text{O}_z/\text{SBA-15}$) by Raman, XRD, HRTEM and XANES analysis. SBA-15 was chosen as a support material as it provides a high specific surface area and a well-defined pore structure. However as discussed above, the silica framework in SBA-15 has very weak interaction with the MoO_x species leading to the formation of bulk MoO_3 even at low Mo concentrations. This leads to the postulation that incorporation of Ti and Zr individually and also together in the mesoporous network of SBA-15 to overcome the disadvantages such as low metal support interactions and the corresponding dispersion. The proposed catalyst is presumed to have multifold advantages such as surface area, availability of a large variety of pore sizes, variable surface functional groups, better metal support interactions and the corresponding dispersions. The purpose of this paper is to study the effect of hetero atom such as Zr and Ti on the dispersion and formation of Ni and Mo on the support and their corresponding interactions and activity correlations.

2. Experimental methods and materials

2.1. Materials

Reference compounds molybdenum sulfide (MoS_2), nickel sulfide (Ni_3S_2), NiO, NiMoO_4 , MoO_3 and Ammonium heptamolybdate were obtained from Aldrich (>99% pure). The materials used in catalyst synthesis are: P123, tetraethyl orthosilicate (TEOS), hexane, NH_4F , zirconium oxychloride, titanium isopropoxide, nickel nitrate and ammonium heptamolybdate were obtained from Aldrich.

2.2. Catalyst synthesis

Synthesis of Si-SBA-15 was carried out by hydrothermal method using TEOS as silica source and (ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123) as structure directing agent. In a typical synthesis process, 9.28 g of P123 was added to 228.6 g of water. After stirring for a few hours, a clear solution was obtained. Thereafter, 4.54 g of HCl (37%) was added and the solution was stirred for another 2 h. Then, 20.6 g of TEOS was added, and the resulting mixture was stirred for 24 h at 40 °C. The resulting gel was transferred to the Teflon lined autoclave and kept in an air oven at 100 °C for 48 h. The solid product was recovered by filtration, washed with water several times, and dried overnight at 100 °C. Finally, the product was calcined at 540 °C to remove the template.

M-SBA-15 (M = Zr, Ti) were synthesized using optimum synthesis conditions obtained from our earlier research [44,45]. Zr-SBA-15 was synthesized using block copolymer template P123 as pore

directing agent, TEOS as silica precursor, and ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) as zirconia precursor. In the synthesis condition atomic ratio of following chemicals was used – P123:Si:Zr:H₂O = 0.017:1.0:0.04:220. The targeted Si/Zr molar ratio is 25. The mixture was stirred at 35 °C for 24 h. After that the mixture was transferred into Teflon lined autoclave and was kept for aging at 130 °C for 48 h. The product was filtered and washed with DM water and dried at 50 °C. Finally the material was calcined at 500 °C for 5 h.

Ti-SBA-15 support was synthesized using P123 as a structure-directing agent, titanium isopropoxide and TEOS as titanium and silica sources respectively. In a typical synthesis, 9.28 g of pluronic P123 was added to 228.6 g of water. After stirring for a few hours, a clear solution was obtained. Thereafter, 4.54 g of HCl (37%) was added and the solution was stirred for another 2 h. Then, 20.6 g of TEOS and the required amount of the Ti (Si/Ti molar ratio = 25) source were added, and the resulting mixture was stirred for 24 h at 40 °C. The resulting gel was transferred to the Teflon lined autoclave and kept in an air oven at 100 °C for 48 h. The solid product was recovered by filtration, washed with water several times, and dried overnight at 100 °C. Finally, the product was calcined at 540 °C to remove the template.

ZrTi-SBA-15 was synthesized using the same procedure used for Ti-SBA-15 synthesis except that the total Si/Zr + Ti molar ratio is 25. The percentage of Mo in the catalyst is fixed at 13% as the monolayer coverage completes over 10% of Mo. Since, heteropoly-molybdates are formed only above monolayer dispersion, 13% Mo was used in the present study. Commercial catalysts also contains near to 13% of Mo in their composition. The NiMo/TiSBA-15 (2.5 wt% Ni and 13 wt% Mo) catalysts were prepared through incipient wetness co-impregnation method by using appropriate concentration of ammonium heptamolybdate and nickel nitrate. The impregnated samples were dried at 120 °C for 5 h and then calcined at 500 °C for 5 h in air.

2.3. Characterization techniques

2.3.1. ICP-MS analysis

Quantitative estimation of Si/Al ratio and Ni, Mo concentrations in the samples was performed using inductively coupled plasma – mass spectrometer (ICP-MS). A catalyst sample (0.1 g) was dissolved in concentrated hydrofluoric acid (48–51%) at a temperature of 100–150 °C for 3 days. After cooling, samples were further dissolved in concentrated HNO_3 to ensure the complete dissolution of the metals. The final solution was prepared using 0.2 N HNO_3 and analyzed with a mass spectrometer.

2.3.2. N_2 -adsorption

BET surface area and pore volume of the supports and catalysts were measured by means of the adsorption of N_2 at 77 K. Prior to the analysis, the catalyst was degassed in vacuum at 200 °C until the static pressure remained less than 6.6×10^{-4} Pa.

2.3.3. X-ray diffraction

In small angle X-ray diffraction (SAX), a small amount of each sample was placed in between two sheets of mylar film supported by a metal piece with a hole through it (for transmittance). The sample was placed on a standard goniometer head and the sample was set at the center of the diffractometer. Data was obtained using a still data collection with an exposure time of 300 s. Diffraction data was collected with a Bruker Smart6000 CCD detector on a 3-circle D8 goniometer. The source was a Rigaku RU200 Cu rotating anode generator fitted with parallel focusing cross-coupled mirrors and a 0.5 mm pinhole collimator. The instrument positioning was: $2\theta = 0$, $\omega = -180$, $\varphi = 0$, and $\chi = 54.8^\circ$. The sample to detector distance was 29.48 cm. Calibration was performed using silver behenate. Broad angle powder X-ray diffraction patterns of all the catalysts were

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