

Hydrodesulfurization Reaction: Alumina- Titania Supported Catalysts

Peyman Moradi and Matin Parvari⁺

School of Chemical Engineering, Iran University of Science and Technology, Tehran, Iran.

Abstract. Hydrodesulfurization of dibenzothiophene in a high pressure batch reactor (5.5 MPa) was done on sulfided cobalt- molybdenum supported on alumina titania oxides (CoMoS/Al₂O₃-TiO₂). The effects of titania and preparation procedure were investigated by using X-ray diffraction (XRD) and Brunauer-Emmet-Teller (BET) experiments. The results showed that the catalyst prepared by impregnation method with titanium isopropoxide and γ -Alumina as raw materials (CoMoS/SAT-1) had hydrodesulfurization activity (in pseudo first order kinetic constant basis) value ~1.4 times higher to that of CoMo/Al₂O₃ catalyst.

Keywords: Hydrodesulfurization, preparation method, alumina- titania supports

1. Introduction

Due to strict environmental regulations, a reduction in the maximum allowable sulfur content in a variety of fuels has been an essential need in oil industries. Hydrodesulfurization (HDS) is the main route to gain this aim. Improving catalyst nature is the most economic and promising approach to increase efficiency of this process [1-3]. The conventional catalysts used in hydrodesulfurization usually consist of supported MoS₂ on an alumina promoted by cobalt (or nickel) [4].

Modification of the preparation procedure using different materials as sources for supports is reported as a promising way for improving the activity of the catalysts in the hydrodesulfurization reaction [5-6]. Besides alumina, many other materials have been used as supports for HDS catalysts. Most important of which are as follows: HMS [7], ZrO₂ [8], TiO₂ [9], and SiO₂ [10]. Titania showed high activities as supports in hydrodesulfurization catalysts but some disadvantages of these materials as supports such as low surface area prevented them to be used as industrial supports so combinations of titania with alumina were used.

Considering the above results, studying the effect of supports and preparation procedure seems to be necessary to find high activity catalysts. In the current work, a series of alumina-titania binary mixed oxide, synthesized with different materials (bohemite, aluminum sulfate, titanium isopropoxides, and titanium chloride), was used as supports for CoMoS. Finally the role of supports was investigated for hydrodesulfurization (HDS) of dibenzothiophene (DBT) in a high pressure batch reactor.

2. Experimental

2.1. Support and catalyst preparation

A series of TiO₂-Al₂O₃ binary oxide supports in which the composition of TiO₂ was kept low (i.e. 10 wt. %) were prepared by different methods:

1. The γ -Alumina was impregnated by using an appropriate amount of titanium isopropoxide solution in 1-propanol. After that, the sample was dried at room temperature overnight, at 120 °C for 24 h and was finally calcined at 500 °C for 7 h. Hereafter, this support will be known as SAT-1.

⁺ Corresponding author. Tel.: + 989123169161; fax: + (98) (21) 7724-0495
E-mail address: parvari@iust.ac.ir

2. Aqueous solutions of aluminum sulfate and titanium chloride were mixed together at 95 °C for 1 h at pH=2.5 and for 2 h at pH=7-8 to make a slurry. To regulate the pH of the mixture, a solution of ammonium hydroxide was used. The slurry was filtered and washed ten times. The resulting precipitate was dried at room temperature overnight, then dried and calcined using the same conditions as for support SAT-1. Hereafter, this support will be known as SAT-2.

3. A commercial boehmite was impregnated with an appropriate amount of titanium isopropoxide solution in 1-propanol and was then dried and calcined using the same conditions as for support SAT-1. Hereafter, this support will be known as SAT-3.

All carriers were co-impregnated with aqueous solutions of ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$), and cobalt nitrate ($\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$). In all samples, the same amounts of cobalt oxide and molybdenum oxide, 3.5 and 18 wt%, respectively, were used for the catalyst networks. After impregnation, the samples were dried at room temperature and 120 °C overnight and calcined at 550 °C for 4 h.

2.2. Catalyst characterization

The specific surface area (S_{BET}), pore volumes, and pore size measurements were carried out in a Quantachrome Nova 2000 apparatus. Prior to the adsorption, the supports were outgassed at 300 °C for 3 h. X-ray diffraction (XRD) patterns were collected on a Philips PW1800 diffractometer using $\text{Cu K}\alpha$ radiation.

2.3. Catalyst evaluation

200 mg of each catalyst (with particle size fraction between 125 and 250 μm) was tested on HDS of the model molecule DBT (0.3 g) in a 300 ml batch reactor using n-hexadecane as solvent (100 ml) at 320 °C, 5.5 MPa total pressure in balance hydrogen, and stirring at 1000 rpm. Before the reaction, the catalysts were presulfided in situ in the liquid phase containing an excess amount of dimethyldisulfide (DMDS) (0.4 ml) in tetradecane (60 ml) with respect to the required amount of sulfur to form CoS and MoS₂, at 250 °C and 2.4 MPa for 1 h and at 370 °C and 5.5 MPa for 2 h. The total sulfur in the liquid reaction phase was calculated by the UOP-357 test method. HDS kinetic constants were calculated assuming pseudo-first order kinetics referred to DBT concentration: $k = [-\ln(1-x)]/t$ (x = conversion, t = time)

3. Results and discussions

3.1. X-ray diffraction (XRD) of supports

XRD patterns of the supports are shown in Fig. 1. Three main peaks, at $2\theta=37.6^\circ$, 45.8° and 66.8° , corresponding to γ -Alumina, are observed for all supports indicating that the base phase of all of them is γ -Alumina. A low intensity peak at $2\theta = 25.3^\circ$ is also detected, demonstrating the presence of anatase titania. Other low intensity peaks are related to γ -alumina or anatase titania. However, the intensity of this titania phase having the main peak at $2\theta = 25.3^\circ$, in support SAT-1 is weaker than that observed for SAT-2 and SAT-3, indicating that titania is well-dispersed upon the alumina matrix in support SAT-1.

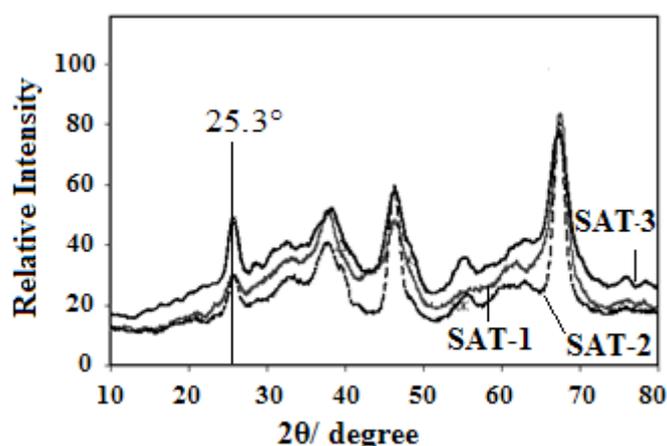


Fig. 1: XRD patterns of the mixed oxide supports

3.2. Textural Properties of supports

The surface areas, pore volumes, and average pore diameters of the supports are presented in table 1 and alumina was used as a reference. In support SAT-1, the specific surface area increased from 228 to 239 m²/g, whereas no noticeable decrease in pore volume and average pore diameter was detected. In support SAT-2, a larger decrease in all of the textural properties is observed so that the specific surface area, the pore volume and the average pore diameter change from 228 to 214 m²/g, 0.420 to 0.391 ml/g, and 6.71 to 6.34 nm, respectively. The incorporation of titania in support SAT-3 causes a slight but clear decrease in the specific surface area, which drops from 228 to 219 m²/g, accompanied by a decrease in the pore volume and the average pore diameter from 0.420 to 0.402 ml/g and from 6.71 to 6.42 nm, respectively.

Table1: Textural properties of the supports

Supports	BET Surface Area (m ² g ⁻¹)	Pore Volume (ml g ⁻¹)	Average pore size (nm)
Alumina	228	0.420	6.71
SAT-1	239	0.433	6.75
SAT-2	214	0.391	6.34
SAT-3	219	0.402	6.42

From these results, it can be inferred that the support preparation method can affect the textural properties and the decrease in the pore volume and the average pore size in supports SAT-2 and SAT-3 may be due to unsuitable dispersion of the titania on the surface of alumina, causing a blockage of the pores in these supports and confirming the results obtained from the XRD analysis.

3.3. Hydrodesulfurization activity

DBT HDS kinetic constants using different catalysts have been presented in Fig. 2. As can be seen in this figure, SAT-1 is the best of the supports and therefore confirms the conclusion drawn from the XRD experiments, namely that the titanium phase is well-dispersed on this support. Consequently, the samples with this support have higher activities than the others. The results showed that the catalyst prepared by impregnation method with titanium isopropoxide and γ -Alumina as raw materials (CoMo/SAT-1) had hydrodesulfurization activity (in pseudo first order kinetic constant basis) value ~ 1.4 times higher to that of CoMo/Al₂O₃ catalyst.

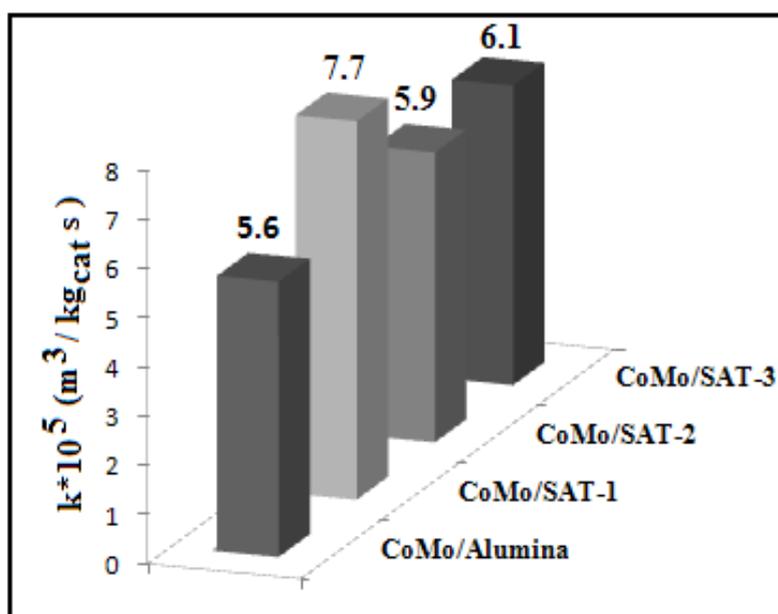


Fig. 2: Pseudo-first order kinetic constant (HDS of DBT) on various sulfided catalyst samples

4. Conclusions

Different alumina-titania mixed oxides prepared with the same titania content but using different preparation methods were used as supports for CoMo catalysts. Among these supports, the best one was SAT-1, which had the highest surface area, well-dispersed titania at the support surface, and the highest activity, as determined from BET, XRD, and activity test experiments.

The DBT HDS kinetic constant over the catalysts (at 320 °C, 5.5 MPa total pressure in balance hydrogen and 1000 rpm, using a batch reactor) increases in the following order of supports: Alumina < SAT-2 < SAT-3 < SAT-1. The catalyst prepared by impregnation method with titanium isopropoxide and γ -Alumina as raw materials (CoMoS/SAT-1) had Hydrodesulfurization activity (in pseudo first order kinetic constant basis) value ~1.4 times higher to that of CoMo/Al₂O₃ catalyst.

5. References

- [1] Q. Huo, T. Dou, Zh. Zhao, H. Pan. Synthesis and application of a novel mesoporous zeolite L in the catalyst for the HDS of FCC gasoline. *Appl. Catal. A* 2010, **381**: 101–108.
- [2] T.-M. Chen, Ch.-M. Wang, I. Wang, T.-Ch. Tsai. Promoter effect of vanadia on Co/Mo/Al₂O₃ catalyst for deep hydrodesulfurization via the hydrogenation reaction pathway. *J. Catal.* 2010, **272**: 28–36.
- [3] T. Zheng-li, X. Hui-ning, Zh. Run-duo, Zh. Zi-Sheng, S. Kaliaguine. Potential to use mesoporous carbon as catalyst support for hydrodesulfurization. *New Carbon Matter.* 2009, **24** (4): 333–343.
- [4] B. Delmon. New technical challenges and recent advances in hydrotreatment catalysis. A critical updating review. *Catal. Lett.* 1993, **22** (1-2): 1-32.
- [5] J. Vakros, A. Lycourghiotis, G.A. Voyiatzis, A. Siokou, Ch. Kordulis. CoMo/Al₂O₃-SiO₂ catalysts prepared by co-equilibrium deposition filtration: Characterization and catalytic behavior for the hydrodesulphurization of thiophene. *Appl. Catal., B* 2010, **96**: 496- 507.
- [6] S. A. Giraldo, A. Centeno. Isomerization and cracking under HDS conditions using γ -alumina modified with boron as catalysts support. *Catal. Today* 2008, **133–135**: 255-260.
- [7] T. Chiranjeevi, P. Kumar, M. S. Rana, G. Murali Dhar, T. S. R. Prasada Rao. Physico-chemical characterization and catalysis on mesoporous Al-HMS supported molybdenum hydrotreating catalysts. *J. Mol. Catal. A: Chem.* 2002, **181**: 109–117.
- [8] S. K. Maity, M.S.R., B. N. Srinivas, S. K. Bej, G. Murali Dhar, T. S. R. Prasada Rao. Characterization and evaluation of ZrO₂ supported hydrotreating catalysts. *J. Mol. Catal. A* 2000, **153**: 121-127.
- [9] A. K. Datye, S.S., L. F. Allard, C. H. F. Peden, J. R. Brenner, L. T. Thompson. Oxide Supported MoS₂ Catalysts of Unusual Morphology. *J. Catal.* 1996, **158** (1): 205- 216.
- [10] A.M. Venezia, R. Murania, G. Pantaleo, V. La Parola, S. Scire, G. Deganello. Combined effect of noble metals (Pd, Au) and support properties on HDS activity of Co/SiO₂ catalysts. *Appl. Catal., A* 2009, **353**: 296-304.