

HDS: Alumina- Boria Supported Catalysts

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Abstract—Hydrodesulfurization (HDS) of dibenzothiophene (DBT) in a high pressure batch reactor was done at 320 °C on CoMoS/Al₂O₃-B₂O₃ (4, 10, and 16 wt. % of Boria) using n-hexadecane as solvent, dimethyldisulfide (DMDS) in tetradecane as sulfur agent, and stirring at 1000 rpm. The effects of boria were investigated by using X-ray diffraction (XRD), Temperature programmed desorption (TPD) of ammonia, and Brunauer-Emmet-Teller (BET) experiments. The results showed that the catalyst prepared with low boria content (4 wt. %) had HDS activity (in pseudo first order kinetic constant basis) value ~1.45 times higher to that of CoMoS/Al₂O₃ catalyst.

Keywords—Alumina-boria mixed oxides, dibenzothiophene, hydrodesulfurization.

I. INTRODUCTION

DUE to drastic regulations, limiting the sulfur content of fuels has been an urgent need in oil industries. Improving catalyst nature is the most promising approach to increase efficiency of Hydrodesulfurization (HDS) reaction which is the main process to remove sulfur from oil products [1]-[6].

The conventional catalysts used in hydrodesulfurization usually consist of supported MoS₂ on an alumina promoted by cobalt (or nickel) [4]. Besides alumina, other oxides have also been used as supports for hydrodesulfurization catalysts. Most important of which are as follows: B₂O₃ [7], TiO₂ [8], ZrO₂ [9], and HMS [10]. Titania, boria, and zirconia showed high activities as supports in hydrodesulfurization catalysts but some disadvantages of these oxides as supports such as low surface area and thermal stability prevented them to be used as industrial supports. Therefore, in order to overcome these defects, combinations of the mixed oxides with alumina were used.

In this work, a series of alumina-boria binary mixed oxide, prepared with different B₂O₃ loading (4, 10, and 16 wt. %), was used as supports for CoMoS, and the role of B₂O₃ loading in the supports was investigated for hydrodesulfurization of dibenzothiophene in a high pressure batch reactor.

II. EXPERIMENTAL

A. Support and Catalyst Preparation

A series of boria-alumina binary oxide supports with boria content of 4, 10, and 16 wt. %, labeled C₁, C₂, and C₃

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respectively, was prepared with impregnation method using γ -Alumina and boric acid (H₃BO₃). After impregnation, the resulted matter was dried at 120 °C for 24 h and calcined at 500 °C for 7 h.

All supports were co-impregnated with aqueous solutions of ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O) and cobalt nitrate (Co (NO₃)₂·6H₂O). 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 drying at 120°C, the samples were calcined at 550 °C for 4 h.

B. Catalyst Characterization

X-ray diffraction (XRD) patterns were collected on a Philips PW1800 diffractometer using Cu K α radiation. The specific surface area (S_{BET}) and pore volume measurements were carried out in a Quantachrome Nova 2000 apparatus. Prior to the adsorption, the supports were outgassed at 300 °C for 3 h. The temperature programmed desorption (TPD) of ammonia was performed using a Quantachrome Model Pulsechemisorb 270S in order to determine the acidic properties of the supports. Before starting the TPD, the samples were heated in a flow of Helium at a flow rate of 50 ml/min and a heating rate of 10 °C/min up to 300 °C, holding this temperature for 2 h then cooling to room temperature with the same flow rate of He. Finally, the TPD_{NH₃} was carried out using the following conditions: heating rate 10 °C/min, flow rate 50 cm³/min, temperature range 50–650 °C.

C. Catalyst Evaluation

200 mg of each catalyst (with particle size fraction between 125 and 250 μ m) 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, and stirring at 1000 rpm. Before the reaction, the catalysts were presulfided in situ in the liquid phase containing dimethyldisulfide (DMDS) (0.4 ml) in tetradecane (60 ml) 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:

$$k = [-\ln(1 - x)] / t \quad (1)$$

(x = conversion, t = time)

III. RESULTS AND DISCUSSIONS

A. X-Ray Diffraction (XRD) of Supports

XRD diffraction patterns of alumina-boria mixed oxide

supports are presented in Fig 1. For the supports with 4 and 10 wt% B_2O_3 contents (supports C_1 and C_2), the XRD patterns exhibit only diffraction peaks characteristic of $\gamma-Al_2O_3$. At 16 wt. % B_2O_3 (in support C_3), a crystalline B_2O_3 phase ($2\theta=27.8^\circ$ and $2\theta=14.6^\circ$) appears. When the loading of B_2O_3 is low, B_2O_3 may form monolayers surrounding the $\gamma-Al_2O_3$ particles and become multiple layers with the further loading of B_2O_3 when the loading of B_2O_3 reaches 16 wt%, the dispersion of boron decreases.

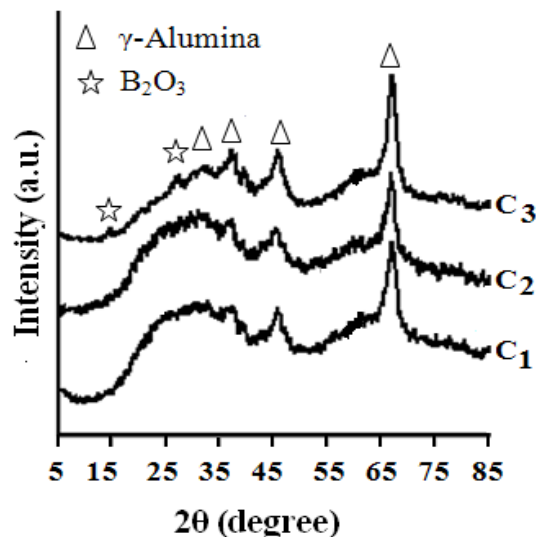


Fig. 1 XRD patterns of the mixed oxide supports

B. Textural Properties of Supports

The surface areas, and pore volumes of the supports are presented in table I and alumina was used as a reference. In all supports, the specific surface area and pore volume were decreased by increasing loading of boria in the supports which can be due to the blocking the pores of the alumina by B_2O_3 species.

TABLE I
TEXTURAL PROPERTIES OF THE SUPPORTS

Support	BET Surface Area ($m^2 g^{-1}$)	Total acidity, $m.mol NH_3 g^{-1}$	Pore Volume ($ml g^{-1}$)
Alumina	228	0.878	0.420
C_1	223	1.842	0.401
C_2	212	2.424	0.370
C_3	204	2.934	0.313

Temperature programmed desorption (TPD) of ammonia was used to measure the acidic properties of the supports. The total amount of acidity has been listed in table I showing the acidity amount has been increased by addition of boron and the acid sites can facilitate cleavage of C-S bond in direct desulfurization pathway by providing a proton to remove sulfur easier from the thiophenic ring of dibenzothiophene

which improves hydrodesulfurization activity of the catalysts.

C. Hydrodesulfurization Activity

Kinetic constants of dibenzothiophene hydrodesulfurization using different catalyst samples have been presented in Fig. 2. As it is clear in this figure, C_1 is the best of the supports improving activity a lot comparing to other supports.

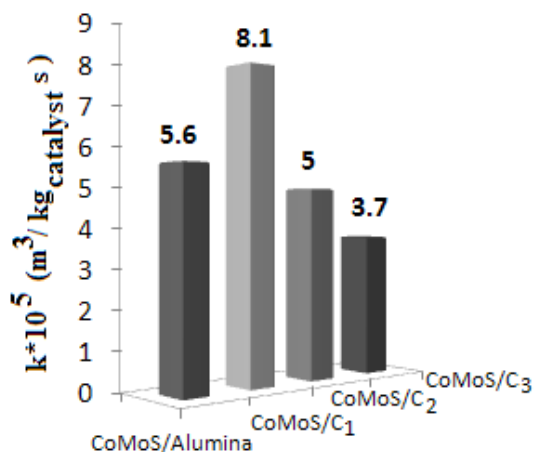


Fig. 2 Pseudo-first order kinetic constant (dibenzothiophene hydro desulfurization)

TPD_{NH3} results showed increasing acidity of the carriers with increasing B_2O_3 loading on the parent alumina support which improves hydrodesulfurization activity of the catalysts. Meanwhile the conclusions drawn from the XRD and BET experiments showed the increasing the B_2O_3 loading more than 4 wt. % causes reducing distribution of B_2O_3 , surface areas and pore volumes of the mixed oxide supports which results in losing activities of the catalysts. From above, the optimum boria content is 4 wt. % which results to have a proper support (C_1) having high specific surface area and acidity.

IV. CONCLUSIONS

CoMoS catalysts supported on alumina- boria mixed oxides with different boria loading (4, 10, and 16 wt. %) were synthesized. Among the mixed oxide supports, the best one was C_1 , which had the highest surface area and pore volume, well-dispersed boria at the support surface, proper acidity, and the highest activity, as determined from BET, XRD, TPD_{NH3}, and activity test experiments.

The HDS kinetic constant over the catalysts increases in the following order of supports: $C_3 < C_2 < Al_2O_3 < C_1$. Finally, the results showed that the catalyst prepared with low boria content (4 wt. %) had HDS activity (in pseudo first order kinetic constant basis) value ~1.45 times higher to that of CoMoS/ Al_2O_3 catalyst.

REFERENCES

- [1] Q. Huo, T. Dou, Zh. Zhao, and H. Pan, "Synthesis and application of a novel mesoporous zeolite L in the catalyst for the HDS of FCC gasoline," Appl. Catal. A, vol. 381, pp. 101–108, 2010.

- [2] T.-M. Chen, Ch.-M. Wang, I. Wang, and T.-Ch. Tsai, "Promoter effect of vanadia on Co/Mo/Al₂O₃ catalyst for deep hydrodesulfurization via the hydrogenation reaction pathway," *J. Catal.*, vol. 272, pp. 28–36, 2010.
- [3] T. Zheng-li, X. Hui-ning, Zh. Run-duo, Zh. Zi-Sheng, and S. Kaliaguine, "Potential to use mesoporous carbon as catalyst support for hydrodesulfurization," *New Carbon Matter*, vol. 24, no. 4, pp. 333–343, 2009.
- [4] B. Delmon, "New technical challenges and recent advances in hydrotreatment catalysis. A critical updating review," *Catal. Lett.*, vol. 22, no. 1-2, pp. 1-32, 1993.
- [5] J. Vakros, A. Lycourghiotis, G.A. Voyatzis, A. Siokou, and Ch. Kordulis, "CoMo/Al₂O₃-SiO₂ catalysts prepared by co-equilibrium deposition filtration: Characterization and catalytic behavior for the hydrodesulfurization of thiophene," *Appl. Catal., B*, vol. 96, pp. 496-507, 2010.
- [6] S. A. Giraldo, and A. Centeno, "Isomerization and cracking under HDS conditions using g-alumina modified with boron as catalysts support," *Catal. Today*, vol. 133–135, pp. 255-260, 2008.
- [7] Y.-W. Chen, and M.-Ch. Tsai, "Hydrotreating of residue oil over aluminum borate-supported CoMo and NiMo catalysts," *Catal. Today*, vol. 50, pp. 57-61, 1999.
- [8] 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.*, vol. 158, no.1, pp. 205- 216, 1996.
- [9] 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*, vol. 153, pp. 121-127, 2000.
- [10] 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.*, vol. 181, pp. 109–117, 2002.