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/Al_2O_3-B_2O_3 (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/Al_2O_3 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 MoS_2 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: B_2O_3 [7], TiO_2 [8], ZrO_2 [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 B_2O_3 loading (4, 10, and 16 wt. %), was used as supports for CoMoS, and the role of B_2O_3 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 C_1, C_2, and C_3

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respectively, was prepared with impregnation method using γ-Alumina and boric acid (H_3BO_3). 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 ((NH_4)$_6$$Mo_7O_{24}$$4H_2O$) and cobalt nitrate (Co (NO_3)$_2$$6H_2O$). 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 Kα 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 cm^3/min, temperature range 50–650 °C.

C. 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, 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 MoS_2, 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:

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

(x = conversion, t = time)

III. RESULTS AND DISCUSSIONS

A. X-Ray Diffraction (XRD) of Supports

XRD diffraction patterns of alumina-boria mixed oxide

World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:5, No:4, 2011

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 γ-Al_2O_3. At 16 wt. % B_2O_3 (in support C_3), a crystalline B_2O_3 phase ($2\theta=27.8°$ and $2\theta=14.6°$) appears. When the loading of B_2O_3 is low, B_2O_3 may form monolayers surrounding the γ-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.
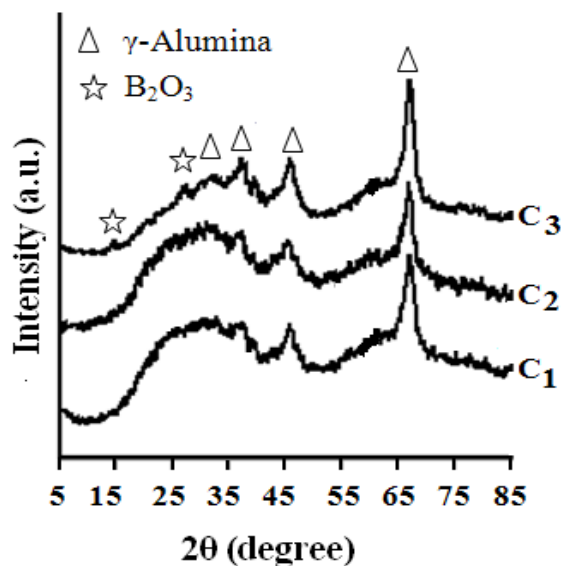

Fig. 1 XRD patterns of the mixed oxide supports

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.
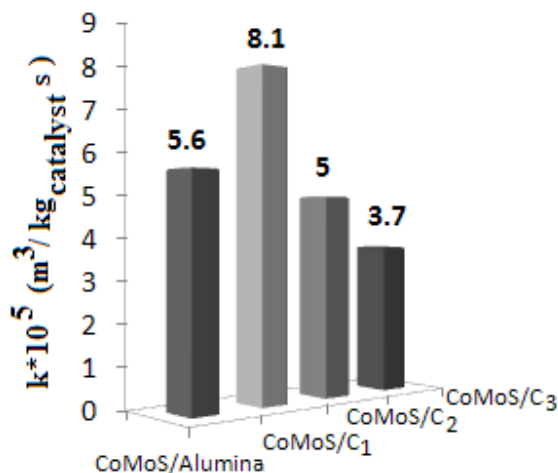

Fig. 2 Pseudo-first order kinetic constant (dibenzothiophene hydro desulfurization)

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.

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World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:5, No:4, 2011

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