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## Activity of CoMo/MSA catalysts in benzothiophene hydrodesulfurization, cumene cracking and cyclohexene isomerization

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### Abstract

The mesoporous silica-alumina (SA) was modified by acid leaching and studied as an alternative support for Mo and CoMo catalysts for hydrodesulfurization (HDS) of benzothiophene. The supports were characterized by N<sub>2</sub> adsorption, XRD, 27Al MAS NMR, electron microscopy (SEM, HRTEM) and their acidity were compared in cyclohexene isomerization and cumene cracking. The composition of catalysts were determined by ICP. Progressive leaching of the parent SA containing 52 wt.% Al<sub>2</sub>O<sub>3</sub> (SA52) led to decrease of Al<sub>2</sub>O<sub>3</sub> content (33 and 19 wt.% in MSA33 and MSA19 support, respectively). This decrease was accompanied with an increase of the BET surface area and exposition of strong acidity. The acid leaching positively affected the activities of the sulfided CoMo catalysts in the benzothiophene HDS, which were slightly above the activity of an industrial reference CoMo catalyst supported on gamma-Al<sub>2</sub>O<sub>3</sub>.

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*Keywords:* CoMo catalyst; silica-alumina; hydrodesulfurization; benzothiophene

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## 1. Introduction

Hydrodesulfurization (HDS) catalysts recently challenge strong regulations of sulfur content in liquid fuels. New supports are therefore investigated as an alternative to conventionally used gamma-Al<sub>2</sub>O<sub>3</sub> to achieve more efficient catalysts or catalysts with new function. Among them, the silica-alumina possesses interesting features due to its acidity, which is generally beneficial for HDS. Thus, the properties of this SA have further been optimized with this aim. Only limited fraction of alumina can be incorporated into the SiO<sub>4</sub> matrix and its additional part remains free. It was assumed that such free non-acidic alumina restrains the accessibility of Brønsted acid sites of silica-alumina which could be better exposed after proper unblocking. For this purpose, extraction of alumina by diluted nitric acid was selected as a possible route.

## 2. Experimental

We have investigated amorphous silica-alumina with Al<sub>2</sub>O<sub>3</sub> content equal to 52 wt. % (SA52), which was synthesized by cogelification from aqueous solutions of sodium metasilicate and aluminium nitrate [1]. The SA52 was then modified with nitric acid to decrease the Al<sub>2</sub>O<sub>3</sub> content to 33 and 19 wt. % (MSA33, MSA19), which was monitored by electron probe microanalyser in scanning electron microscopy mode (SEM).

The prepared supports and the pure SiO<sub>2</sub> were allowed to react with aqueous slurry of MoO<sub>3</sub> at 95 °C for 8 h. The unreacted slurry was removed from the support and the sample was sulfided in the mixture of hydrogen and hydrogen sulfide at 400 °C. Parts of the sulfided catalysts were impregnated from methanolic solution of cobalt acetylacetonate to achieve molar ratio Co/(Co+Mo) = 0.3 and resulfided.

The selected supports and catalysts were characterized by ICP/AAS, XRD, N<sub>2</sub> physisorption [2] and O<sub>2</sub> chemisorption [3]. The properties of supports and catalysts are given in Table 1.

In fixed-bed flow microreactors, the acidity of the support and the CoMo catalysts were determined by cyclohexene isomerization (240 °C, 0.5 MPa of H<sub>2</sub>) and cumene cracking (400 °C, 0.5 MPa of H<sub>2</sub>) and the activity of Mo and CoMo catalysts were determined by 1-benzothiophene (BT) HDS at 360 °C and 1.6 MPa of H<sub>2</sub>.

Table 1. Properties of supports and Mo and CoMo catalysts

| Support or catalyst | wt.% Al <sub>2</sub> O <sub>3</sub> | wt.% Mo | wt.% Co | S <sub>BET</sub> (m <sup>2</sup> /g) | Dispersion (mmol <sub>O2</sub> /mol <sub>Mo</sub> ) |
|---------------------|-------------------------------------|---------|---------|--------------------------------------|---|
| SA52                | 52                                  | -       | -       | 429                                  | -   |
| MSA33               | 33                                  | -       | -       | 580                                  | -   |
| MSA19               | 19                                  | -       | -       | 600                                  | -   |
| Mo/SA52             | 33                                  | 11.4    | -       | 252                                  | 21.6  |
| Mo/MSA33            | 19                                  | 4.8     | -       | 683                                  | 24.6  |
| Mo/MSA19            | 12                                  | 2.1     | -       | 680                                  | 25.5  |
| CoMo/SA52           | 32                                  | 11.2    | 3.9     | 304                                  | 23.7  |
| CoMo/MSA33          | 19                                  | 4.7     | 2.0     | 455                                  | 27.6  |
| CoMo/MSA19          | 12                                  | 2.1     | 0.9     | 616                                  | 31.6  |

### 3. Results

It was ascertained from the Fig 1 that the leaching of SA52 with nitric acid resulted in ablation of alumina-rich clusters and eroded surface with the cavities smaller than 10  $\mu\text{m}$  in the samples MSA33 and MSA19 in Fig. 1b and Fig. 1c, respectively.

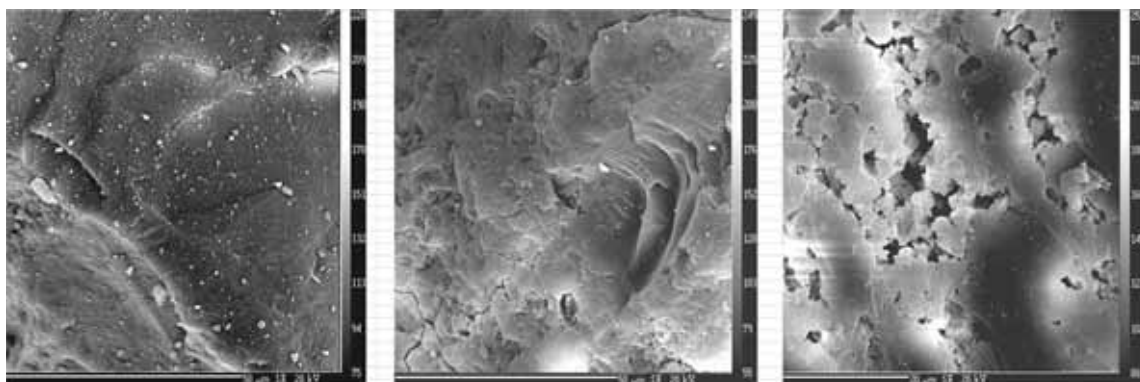


Fig. 1. SEM images of SA52 (a), MSA33 (b) and MSA19 (c); adapted from [4].

Furthermore, it was found that  $\text{MoO}_3$  does not adsorb onto pure  $\text{SiO}_2$  despite its relatively high surface area (400  $\text{m}^2/\text{g}$ ). In contrast, SA52, MSA30, and MSA19 with surface areas 429, 580 and 600  $\text{m}^2/\text{g}$  adsorbed about 17, 7 and 3 wt. % of  $\text{MoO}_3$ , respectively.

The content of  $\text{Al}_2\text{O}_3$  in the SA based materials thus well correlated with the adsorption loadings of  $\text{MoO}_3$  achieved by the saturation experiments. Moreover, it was acquired that the highest dispersion and HDS activities were achieved over catalysts containing dealuminated MSA supports despite of relatively low loadings of Mo (Fig. 2a).

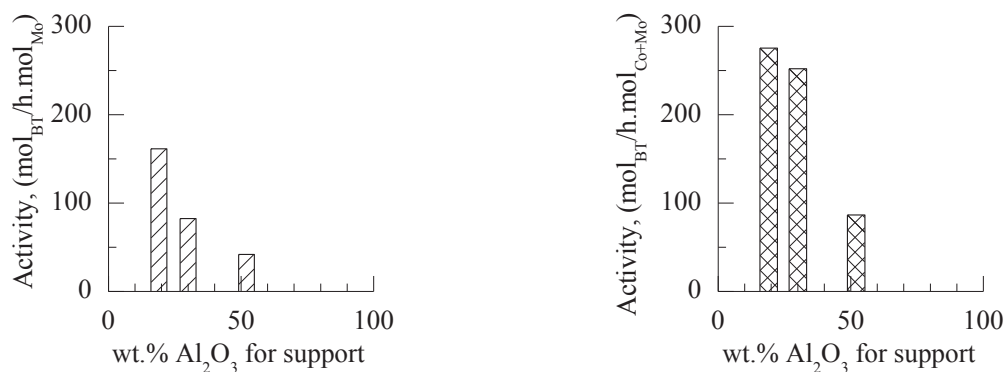


Fig. 2. (a) activity of Mo catalysts; (b) activity of CoMo catalysts

After Co deposition (Fig. 2b), the weight normalized activities in BT HDS increased 2.2 and 4.3 times (the samples CoMo/MSA30 and CoMo/MSA19) reflecting on more effective MoS<sub>2</sub> promotion by Co on more acidic supports. (The intrinsic activity of industrial reference CoMo catalyst was less than prepared CoMo/SA52).

Furthermore, those catalysts keep the high acidities of the original supports, as it was determined by cyclohexene isomerization (Fig. 3a) and cumene cracking (Fig. 3b), while industrial reference CoMo catalysts and gamma-Al<sub>2</sub>O<sub>3</sub> was found to exhibit zero acidity.

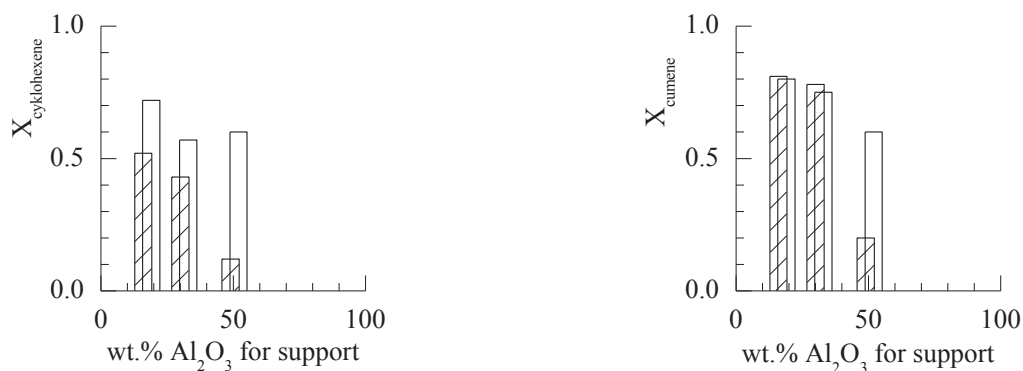


Fig. 3. (a) cyclohexene isomerization of supports (□) and CoMo catalysts (▨); (b) cumene cracking of supports (□) and CoMo catalysts (▨)

It was concluded that higher acidity of the modified MSA carriers substantially improved the activities of Mo and CoMo catalysts in hydrodesulfurization of benzothiophene.

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