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CoMo/ZrO₂ Hydrodesulfurization catalysts prepared by chelating agent assisted spreading

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Increasingly straighten regulations on sulfur level in liquid fuels have been recently driving the research on highly efficient hydrodesulfurization (HDS) catalysts. The conventionally used CoMo catalysts are supported onto gamma-Al₂O₃ and they are prepared by the consecutive or simultaneous impregnation of the support with aqueous solutions of ammonium heptamolybdate and cobalt nitrate followed by calcination and sulfidation. The addition of chelators¹⁻³ such as of nitrilotriacetic acid (NTA) or diethylaminetetraacetic acid (EDTA) into the impregnating solution often resulted in increased HDS activity. We have previously found an alternative method of CoMo deposition using water slurries of low solubility precursors such as molybdenum trioxide and cobalt hydroxide carbonate and applied that method on an alternative support ZrO₂. It was found⁴ that only the monoclinic form of ZrO₂ (107 m²/g, baddeleyite) led to highly active catalysts while the amorphous or the mixture of tetragonal and monoclinic phase led to active catalysts with low HDS activity. The aim of this work is to elucidate on deposition of Co and Mo with the use of the chelating agent NTA onto the monoclinic form of ZrO₂.

The catalysts prepared from ammonium heptamolybdate, molybdenum oxide, cobalt nitrate and cobalt carbonate (3.5 at. Mo/nm², Co/(Co+Mo) = 0.3) were compared in HDS of 1-benzothiophene at 1.6 MPa and characterized by powder X-ray diffraction. The surface areas of sulfided catalysts (SA) were determined by N₂ physisorption by Nelsen and Eggertsen method⁵ and dispersion of the sulfide phase was determined by O₂ chemisorption⁶ (Ads O₂). The prepared catalysts were compared with reference industrial catalysts supported on gamma-Al₂O₃ and their survey is given in Table 1.

It was found⁷ that Mo catalysts supported on ZrO₂ exhibited about 2 times higher dispersion and HDS activity than the Mo catalyst supported on Al₂O₃ (M8-30, BASF, Germany). The use of NTA, however, decreased the MoS₂ dispersion in Mo/ZrO₂ catalyst about 1.6 times despite keeping the 2-fold activity. In bimetallic CoMo catalysts supported on ZrO₂, the concentration of NTA and nature of the starting compounds influenced the resultant HDS activity. The HDS activity was expressed as pseudo first order rate constant of ethylbenzene formation normalized per mol of Mo in Mo catalyst or per mol of Co+Mo in CoMo catalyst. The promotion effect of Co was expressed as a ratio of the activity of Co catalyst and the activity of Mo catalyst. The promotional effect was the lowest for the catalyst prepared by consecutive deposition of ammonium heptamolybdate and cobalt nitrate possessing the value about 2. Applying consecutive deposition from the aqueous slurries of molybdenum oxide and cobalt hydroxide carbonate, the promotional effect increased to 3.1. After employing the NTA, the promotional effects varied within 2.6-4.1 with the maximum activity at optimal NTA : (Co+Mo) ratio 1 : 1. Nevertheless, this activity represented only about 80 % activity of the commercial CoMo/Al₂O₃ catalyst KF 756 (Albemarle, The Netherlands). Because the studied ZrO₂ exhibited only 107 m²/g (i.e. only 40 % of the specific surface area of the industrial catalyst KF 756 with 270 m²/g), it could be expected that further improvement of catalytic activity can be achieved by increasing the surface area of the monoclinic ZrO₂. Higher specific surface should disperse more active phase and so the HDS activity of the alumina supported catalysts would be overwhelmed.

Table 1. Survey of the prepared and reference catalysts.

| Sample | SA (m ² g ⁻¹) | Ads O ₂ (mmol(O ₂)/mol(Me) ^B) | HDS activity (mol(EB)/mol(Me)g) ^B |
|--|---|---|---|
| ZrO ₂ | 108 | 0 | 0 |
| (NH ₄) ₆ Mo ₇ O ₂₄ | 108 | 65 | 51 |
| MoO ₃ | 106 | 75 | 58 |
| MoO ₃ +NTA | 119 | 41 | 54 |
| Co(NO ₃) ₂ +(NH ₄) ₆ Mo ₇ O ₂₄ | 94 | 31 | 107 |
| CoCO ₃ +MoO ₃ | 116 | 72 | 182 |
| Co(NO ₃) ₂ +(NH ₄) ₆ Mo ₇ O ₂₄ +NTA ^A | 100 | 64 | 144 |
| Co(NO ₃) ₂ +(NH ₄) ₆ Mo ₇ O ₂₄ +NTA | 114 | 55 | 181 |
| CoCO ₃ +MoO ₃ +NTA | 108 | 60 | 222 |
| Mo/Al ₂ O ₃ | 121 | 16 | 27 |
| CoMo/Al ₂ O ₃ | - | 22 | 282 |

^A NTA : Co molar ratio was 1 : 1

^B Me represents Mo or Co+Mo in the Mo or CoMo catalysts, respectively

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