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THE INCREASED PROMOTION IN COBALT-MOLYBDENUM  
HYDRODESULFURIZATION CATALYSTS SUPPORTED ON ALUMINA,  
ACTIVATED CARBON AND ZIRCONIA BY THE CHELATING AGENT  
NITRILOTRIACETIC ACID

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Increasingly stringent regulations on sulfur level in liquid fuels drive the research on highly active hydrodesulfurization (HDS) catalysts. The conventional CoMo catalysts are supported onto  $\gamma\text{-Al}_2\text{O}_3$  and they are mostly prepared by consecutive deposition of ammonium heptamolybdate and cobalt nitrate followed by calcination and sulfidation. Alternatively, chelating agent such as nitrilotriacetic acid (NTA) is employed during the preparation to increase the HDS activity. In the present paper, a new method based on impregnation of unconventional supports (i.e. activated carbon and  $\text{ZrO}_2$ ) by the NTA assisted spreading of molybdenum trioxide with cobalt carbonate, or ammonium heptamolybdate with cobalt carbonate was investigated. The selected prepared catalysts were characterized by X-ray diffraction,  $\text{N}_2$  physisorption,  $\text{O}_2$  chemisorption and activity in HDS reaction in the gas phase of thiophene (TH) at 1.0 MPa and 400 °C or 1-benzothiophene (BT) at 1.6 MPa and 360 °C. The promotion effect of Co was expressed as ratio of activity of CoMo catalyst and its Mo counterpart. It was found that NTA dissolved the low soluble precursors ( $\text{MoO}_3$  with  $\text{CoCO}_3$  or the mixture of ammonium heptamolybdate with  $\text{CoCO}_3$ ) at NTA/(Co+Mo) molar ratio of 0.3-1.0/1.0, which allowed the deposition of the compounds onto the supports by impregnation. The support effect was ascertained to be the main factor governing the activity of Mo and CoMo catalysts. The carbon supported Mo and CoMo catalysts exhibited more than 2 times higher HDS activities than their  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  supported counterparts. The employing of the chelating agent nitrilotriacetic acid in the preparation of the CoMo catalysts supported on  $\gamma\text{-Al}_2\text{O}_3$ , activated carbon, and monoclinic- $\text{ZrO}_2$  systematically increased the promotion effect of Co in hydrodesulfurization reaction of thiophene and benzothiophene at high pressure by the factor 1.13-1.58. The most active CoMo/ $\text{Al}_2\text{O}_3$ , C and  $\text{ZrO}_2$  catalysts in benzothiophene HDS were prepared by the impregnation of the support from the solution made by dissolution of  $\text{MoO}_3$ ,  $\text{CoCO}_3$  and nitrilotriacetic acid in water followed by sulfidation without previous calcination. The optimal molar ratio NTA/(Co+Mo) to achieve high hydrodesulfurization activities was 1/1. Authors gratefully acknowledge the Albemarle Company (The Netherlands) and the BASF Company (Germany) for providing reference catalysts and the Czech Science Foundation (grant number P106/11/0902) for the financial support.

**References:**

Kaluža, L.; Zdražil, M.; Gulková, D.; Vít, Z. *Chemical Engineering Transactions* **2013**, 32, 841-846.