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## Hydrodesulfurization CoMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/C catalysts prepared with nitrilotriacetic acid without use of NH<sub>4</sub>OH

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The CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst modified with nitrilotriacetic acid (NTA catalyst) was prepared by the common procedure, well known in the literature, using excess of NH<sub>4</sub>OH in the impregnation solution. The using of NH<sub>4</sub>OH was believed indispensable in the literature, because NTA is insoluble in water (pH of its slurry in water is 2.1) and it is only little soluble at pH of 5-7 (pH of Co(NO<sub>3</sub>)<sub>2</sub> solution is about 5.5 and pH of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> solution is about 6). Just as in the literature, the catalyst was not calcined before sulfidation. Its activity in HDS of thiophene (TH) was measured at increased pressure of 1.0 MPa and temperature of 400 °C. The positive NTA effect of 1.37 (ratio of activities with and without NTA) falls into the range of 0.75-2.62 reported by previous authors, who tested the catalysts in TH HDS at atmospheric pressure.

The impregnation solution for NTA catalysts was then newly prepared without NH<sub>4</sub>OH. Practically insoluble CoCO<sub>3</sub>.xH<sub>2</sub>O (pH of its slurry in water is 8.3) was used instead of usual, well soluble Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O. It was found that the two separately insoluble compounds NTA and CoCO<sub>3</sub>.xH<sub>2</sub>O easily dissolved in joint aqueous slurry forming well soluble Co-NTA complex (CO<sub>2</sub> was released from the slurry). (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> was added and the impregnation solution containing all three components, NTA, Co and Mo, was obtained. Its pH was 2.3-3.8, depending on the molar NTA/Mo ratio, which was 1.0-3.2. The NTA CoMo/Al<sub>2</sub>O<sub>3</sub> prepared with this solution (NTA/Mo=1.2) exhibited NTA effect of 1.54, which was reliably higher than the value of 1.37 mentioned above. Similar behaviour was observed for CoMo/C catalysts ("C" is for active carbon); the NTA effect was 1.23 and 1.36 with and without NH<sub>4</sub>OH, respectively. It was concluded that the use of large amount of volatile, corrosive and toxic NH<sub>4</sub>OH is at all not needed.

The positive NTA effect was also found for promoter free Mo/Al<sub>2</sub>O<sub>3</sub> and Mo/C catalysts without NH<sub>4</sub>OH; the values were 1.24 and 1.19, respectively. The positive NTA effect vanished in calcined NTA catalysts Mo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub>, independently whether NH<sub>4</sub>OH was used or not.

We have calculated and experimentally confirmed that in the catalysts without NTA before sulfidation, the deposited phase takes up only about 5% of the pore volume of Al<sub>2</sub>O<sub>3</sub> support. The deposited Co-Mo-O phase forms a monolayer and all Co-Mo-species are in physical and chemical contact with the support surface. In NTA catalysts before sulfidation, the deposited NTA-Co-Mo phase takes up about 60% of the pore volume of Al<sub>2</sub>O<sub>3</sub>. During sulfidation, the metal-support interaction of the majority of the Co and Mo species is blocked not only "chemically" by their own NTA ligands, but also "physically" by the surrounding supported solid. The majority of deposited solid in dried NTA catalysts is sulfided as if it were in the unsupported form. This leads to different morphology and structure of Co-Mo sulfides as compared with the catalysts without NTA. It was concluded that the overall NTA action is a combination of not only "chemical" effects described in the literature (NTA blocks metal-support and metal-metal interactions, it influences supported phase morphology, it delays sulfidation of promoter, etc.), but also of the above "physical" effect.

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