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INHIBITIVE EFFECT OF PYRIDINE AND TOLUENE ON HDS OF THIOPHENE OVER Mo/Al_2O_3 BASED CATALYSTS

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Hydrodesulfurization (HDS) carried out on conventional $CoMo/Al_2O_3$ sulfide catalysts is known to be strongly inhibited by nitrogen heterocycles and polyaromatic compounds [1]. This undesirable effect, reducing efficiency of catalysts, can be influenced by different factors, related to the composition of catalysts, type and amount of the inhibitor and the way of its adsorption. Recently, we observed that Mo/Al_2O_3 sulfide catalyst promoted by Rh showed in thiophene HDS much better tolerance to the presence of pyridine then $CoMo/Al_2O_3$. It was proposed this was mainly due to the higher C-N bond cleavage activity of the Rh promoted catalyst, which facilitated the removal of inhibitor by hydrodenitrogenation [2]. Pyridine is nitrogen compound possessing both basic and aromatic character. In order to get more information concerning possible role of the aromatic ring in such inhibition, part of experiments was also performed with addition of toluene. Toluene was chosen because of similar molecular size to pyridine and non-basic character. The aim was to compare the inhibitive effects of pyridine and toluene on thiophene HDS over Mo/Al_2O_3 catalysts promoted by Co and Rh.

The catalysts contained 9 % Mo and 2.4 % Co (or 0.36 % Rh). The Rh promoted catalyst was prepared by impregnation of sulfided Mo/Al_2O_3 by Rh acetylacetonate. Catalysts were sulfided by 10 % H_2S/H_2 at 400°C/1h. The HDS was carried out at 320°C and 20 bar in an integral flow reactor. The feed contained either thiophene or mixture of thiophene and pyridine (or thiophene and toluene).

It was found that HDS activities of Mo and CoMo catalysts were strongly inhibited by pyridine and activity of RhMo catalyst was inhibited less. On the other hand, suppression of HDS by toluene over Mo catalyst was very small and no suppression by toluene was observed over the promoted CoMo and RhMo catalysts. This suggests that aromatic character of inhibitor does not play an important role and the inhibition of thiophene HDS by pyridine is caused by its basicity, leading to strong pyridine adsorption on catalytic sites through nitrogen atom.

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References:

[1] Topsøe, H; Clausen, B.S.; Massoth, F.E.; in: J.R. Anderson and M. Boudart (Eds.), Hydrotreating Catalysis, Science and Technology, Springer, **1996**, Vol. 11.
[2] Vít, Z.; Kaluža, L.; Gulková, D.; Top. Catal., **2011**, in press.