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Nitrilotriacetic acid assisted deposition of cobalt carbonate for the preparation of niobia supported CoMo hydrodesulfurization catalysts

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Evaluation of new supports alternative to alumina, for instance ZrO_2 , TiO_2 , active carbon or zeolites, is the important topic of recent research on hydrodesulfurization, HDS, catalysts. Nb_2O_5 also was among materials studied but it is rather a special case. It was investigated as the support of Mo and Co(Ni)Mo sulfides, but also as the precursor of active phase, niobium sulfide.

Surface area activity, $A(m^2)$ (activity per $1 m^2$), of Nb_2O_5 supported Mo and Co(Ni)Mo catalysts reported in the literature was comparable or even better than that of Al_2O_3 supported catalysts. However, this only is of academic interest because weight activity, $A(g)$ (activity per 1 g), is important for application. Surface area, S_{BET} , of Nb_2O_5 supported catalysts was always much lower than that of Al_2O_3 supported catalysts. The relative activity $A(g)$ of Nb_2O_5 to Al_2O_3 supported Mo and Co(Ni)Mo catalysts thus was very low, only about 0.1 to 0.3.

The positive effect of the chelating agent nitrilotriacetic acid, NTA, in the preparation of supported catalysts by impregnation (not only of HDS catalysts) is a known phenomenon. As for HDS, it was studied for Mo and Co(Ni)Mo catalysts supported on SiO_2 , Al_2O_3 , TiO_2 and active carbon; for partial review see ref. below and the references therein. However, the application of NTA in the preparation of Nb_2O_5 supported CoMo sulfide catalysts has not been reported previously. The first new result of the present work is that with the use of NTA, we prepared CoMo/ Nb_2O_5 catalyst, which was better than CoMo/ Al_2O_3 catalyst not only in $A(m^2)$ but also in $A(g)$; see Fig. 1.

The second novelty of the present paper concerns the preparation of the impregnation solution. In order to dissolve all components, NTA+ MoO_3 +CoO, large amount of NH_4OH was always used by previous authors. In the present work, we have prepared the impregnation solution by the new method not using volatile and corrosive NH_4OH . Briefly, NTA is practically insoluble in water (0.13 g/100 ml) and pH of its water suspension is about 2.1. Newly, we applied cobalt carbonate, which is also almost insoluble in water (0.3 g/100 ml) and pH of its water suspension is about 8.3. However, we have found that very low solubilities of NTA and cobalt carbonate were sufficient for their mutual reaction in suspension. Thermodynamic equilibrium between dissolved NTA and Co species is strongly shifted to the side of the NTA-Co complex, which is well soluble. Gradually, all solid NTA and cobalt carbonate dissolved and the solution of the complex NTA-Co of pH = 2.3 was formed. Ammonium heptamolybdate was then added to the suspension of the NTA+Co solution and the excess NTA. The dissolution of ammonium heptamolybdate at low pH is also limited. However, NTA promotes its dissolution by formation of soluble complex. The impregnation solution containing NTA+Co+Mo of natural pH = 2.5 was obtained. It should be noted that some NH_3 was introduced into the impregnation solution in the form of $(NH_4)_6Mo_7O_{24}$ but this amount was much lower than it is typically reported in the literature that use NH_4OH . Furthermore, our impregnation solution did not contain any NO_3^- ions. Formation of $(NH_4)_2S$ during presulfidation was thus radically reduced, which was of especial importance because the NTA prepared catalysts are not calcined and the $(NH_4)_2S$ tend to condensate and cause problems in downstream parts of the activity testing unit.

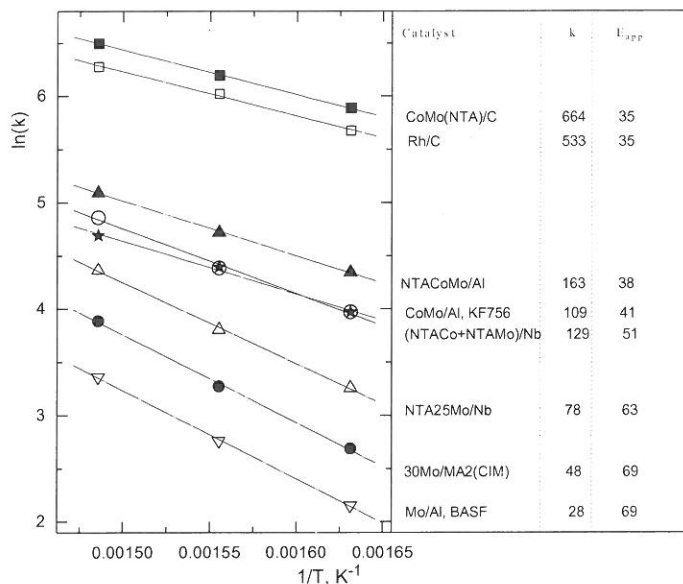


Fig. 1: Context of the activities, k ($\text{mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), and apparent activation energies E_{app} ($\text{kJ}\cdot\text{mol}^{-1}$), comparison of selected catalysts in HDS of thiophene at 400 °C. Supports: Al – conventional alumina, C - active carbon, MA2 - organized mesoporous alumina, Nb - niobia. NTA means that the catalyst was prepared using nitrilotriacetic acid.

It was concluded that nitrilotriacetic acid (NTA) was firstly and successfully applied in the preparation of niobia supported CoMo hydrodesulfurization catalyst in order to improve HDS activity. The solution containing NTA+Co+Mo was newly prepared without the use of volatile and corrosive NH_4OH . The activity in HDS of thiophene of the obtained CoMo/Nb₂O₅ catalyst was compared with the activity of commercial CoMo/Al₂O₃ sample. Nb₂O₅ supported catalyst was better than Al₂O₃ supported counterpart not only in surface area normalized activity (5.7 times), but also in weight normalized activity (1.2 times). The results confirm that the combination of two phenomena, (i) the positive effect of NTA in the preparation of supported catalysts and (ii) high surface area normalized activity of CoMo/Nb₂O₅ HDS catalysts, has great potential for synthesis of extraordinarily active CoMo/Nb₂O₅ hydrodesulfurization catalysts.

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Reference. Kaluža L., Zdražil M.: Relative activity of Niobia-supported CoMo hydrodesulphurization catalyst prepared with NTA: A kinetic approach. *Catalysis Communications* 107 (2018) 62–67.

