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PREPARATION AND RELATIVE ACTIVITY OF NIOBIA-SUPPORTED COMO HYDRODESULFURIZATION CATALYSTS

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Hydrodesulfurization (HDS) is one of the largest heterogeneously catalyzed processes in the present fuel and petrochemical industry. After decades of research and development, the performance (activity, selectivity, price, lifespan, etc.) of sulfide HDS catalysts is at high level. Despite that, evaluation of new supports alternative to alumina is an important topic of recent research into hydrodesulfurization catalysts. Nb₂O₅ was considered as the support of Mo and Co(Ni)Mo sulfides and also as precursor of the active phase, niobium sulfide. The activity expressed per unit surface area (mols m⁻² s⁻¹), coded as A(m²) of Nb₂O₅-supported Mo and Co(Ni)Mo catalysts is comparable or even better than that of Al₂O₃-supported catalysts (Refs. in ¹). This result becomes important when one tries to develop high surface area (m² g⁻¹) supported-Nb₂O₅ catalysts but keeping the same site reactivity as the one obtained with the low surface area Nb₂O₅ support. On the other hand, for realistic applications, the activity per gram basis (mols g⁻¹ s⁻¹) coded as A(g) is that of concern. Surface area, S(BET), of Nb₂O₅-supported catalysts was always much lower than that of Al₂O₃-supported catalysts, and the relative activity A(g) of Nb₂O₅ to Al₂O₃-supported Mo and Co(Ni)Mo catalysts was typically reported to be very low, only about 0.1 to 0.3. A sulfide CoMo/Nb₂O₅ HDS catalyst was successfully and newly prepared using nitrilotriacetic acid (NTA) as complexing agent, where the impregnation solution consisted of NTA, cobalt carbonate and ammonium heptamolybdate. It contained neither NH₄⁺ nor NO₃⁻ auxiliary ions, which is a practical advantage of this green chemistry approach. The hydrodesulfurization activity of the catalyst was tested using thiophene model sulfur compound at 1.0 MPa and 400 °C. The ratio of activity A(g) (based on pseudo-first order kinetics) expressed in terms of the rate constant k, where the latter was estimated from specific reaction rate data per mass of catalyst, for the NTA-CoMo/Nb₂O₅ and CoMo/Nb₂O₅ catalysts was found to be 6.6. Thus, using NTA shifted CoMo/Nb₂O₅ system from low activity catalysts to a high activity catalyst worthwhile for further investigations. The NTA-CoMo/Nb₂O₅ (S(BET) = 40 m² g⁻¹) was more active than commercial CoMo/Al₂O₃ (S(BET) = 194 m² g⁻¹) not only in terms of specific activity normalized per total surface area (A(m²), mols m⁻² s⁻¹, 5.7 times larger) but also in terms of specific activity normalized per mass of catalyst sample (A(g), mols g⁻¹ s⁻¹, 1.2 times larger). The results suggest that the combination of two phenomena, the positive effect of NTA in the preparation of supported niobia catalysts and the high A(m²) activity of CoMo/Nb₂O₅ HDS catalysts, has great potential for the synthesis of very active CoMo/Nb₂O₅ hydrodesulfurization catalysts.

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References:

¹ Kaluža L.; Zdražil M. *Catal. Commun.* **2018**, 107 (2018) 62–67.