Effect of Gallium and Vanadium in $NiMoV/Al_2O_3$-Ga_2O_3 Catalysts on Indole Hydrodenitrogenation

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Abstract

The effect of Ga as support modifier and V as second promoter on the $NiMoV/Al_2O_3$-Ga_2O_3 catalyst varying the synthesis method (SG: sol–gel synthesis vs I: impregnation synthesis) was studied. The catalysts were characterized by elemental analysis, textural properties, XRD, XPS, ^{27}Al NMR, Raman, EDX elemental mapping and HRTEM. The chemical analyses by XRF showed coincidence between experimental and theoretical values according to stoichiometric values proposed to Mo/Ni = 6 and (V + Ni)/(V + Ni + Mo) = 0.35. The sol–gel synthesis method increased the surface area by incorporation of Ga^{3+} ions into the Al_2O_3 forming Ga–O–Al bonding; whereas the impregnation synthesis leads to decrease by blocking of alumina pores, as follows $NiMoV/Al_2O_3$-Ga_2O_3(I) < $NiMoV/Al_2O_3$-Ga_2O_3(SG) < Al_2O_3-Ga_2O_3(I) < $NiMo/Al_2O_3$ < Al_2O_3-Ga_2O_3(SG) < Al_2O_3. The values of BJH mesopores mean size between 6.13 and 7.68 nm. XRD and XPS confirmed a bulk structure typical of $(NH_4)_4[NiMo_6O_{24}H_6]\cdot 5H_2O$ and the presence at the surface of Mo^{4+}, Mo^{6+}, Ni_xS_y, NiMoS, Ni^{2+}, Ga^{3+} and V^{5+} species, respectively. Raman showed that the sol–gel synthesis method reduces the interactions Ni-Mo sulfide-support and improvement the sulfidation degree $NiMoV/Al_2O_3$-Ga_2O_3(SG) as showed sulfur analysis CHONS. The largest proportion of AlO_4 content using the impregnation method to add Ga was verified by ^{27}Al solid-state MAS NMR. The EDS elemental mapping confirmed that Ni, Mo, Al, Ga, V and S are well-distributed on support. The HRTEM analysis shows that the length and stacking distribution of MoS_2 crystallites varied from 5.67 to 6.01 nm and 2.46 to 2.74 when using the sol–gel and impregnation synthesis method, respectively. The catalytic results revealed that the synthesis method induced the presence of gallium on the surface influencing the dispersion V^{5+} species, whose effect could have some relation with strength and density of acid sites that in turn influence the dispersion of the MoS2 phase, which correlates well with

the indole HDN activities. The activities as indole HDN pseudo-first-order rate constants' values (k_{HDN}) from 0.29 to 2.78 mol/(m^2·h): $NiMoV/Al_2O_3$ < $NiMoV/Al_2O_3$-Ga_2O_3(I) < $NiMo/Al_2O_3$ < $NiMoV/Al_2O_3$-Ga_2O_3(SG). Nevertheless, the nature of the active site can be related with reaction pathways, that is, $NiMoV/Al_2O_3$-Ga_2O_3(SG) and $NiMoV/Al_2O_3$-Ga_2O_3(I) catalysts produce ECH through HIND, while $NiMoV/Al_2O_3$ and $NiMo/Al_2O_3$ produce EB by hydrogenolysis of HIND to OEA. In the regard, the Ga and V act as structural promoters in the NiMo catalysts, allowing the largest generation of NiMoS M-edge-like and BRIM sites for HDN.

Keywords

Gallium, Vanadium, Modified al2O3, Synthesis method, Indole hydrodenitrogenation