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Preparation of CoMo/MgO catalysts for hydrodesulfurization

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Hydrodesulfurization (HDS) reactions are conventionally proceeded over gamma-Al₂O₃ supported CoMo, NiMo or NiW sulfides. Alternative supports are intensively studied to increase activity in HDS to meet increasingly stringent regulation on sulfur level in fuels. Particularly, MgO support exhibits higher basicity in comparison to gamma-Al₂O₃, which results in high dispersion and activity of deposited MoS₂, high synergy in CoMo phase and high resistance to coking. These advantages are still insufficiently utilized mainly because of the difficulties with the deposition of CoMo active phase onto hydrothermally little stable surface of MgO. However, we have developed method of the active phase deposition called methanol-assisted spreading that overcomes deterioration of rather unstable MgO support surface during impregnation by aqueous solutions. Reaction of (NH₄)₆Mo₇O₂₄ or MoO₃ with the high surface area MgO in methanol slurry resulted in well-defined saturated Mo monolayer and high activity in HDS of 1-benzothiophene. In the second step, Co was deposited over MoO₃/MgO catalyst from the solution of Co(NO₃)₂ in methanol by impregnation, which resulted in high synergetic effect of Co and about 2-fold increase in activity in benzothiophene HDS than it was observed for conventional gamma-Al₂O₃ support.

The aim of the present work was to elucidate the possibility of deposition of molybdenyl- and cobalt- acetylacetonates on the high surface area MgO by impregnation from solutions of these compounds in methanol. Furthermore, non-aqueous solutions of MoO₃ and CoCO₃, (NH₄)₆Mo₇O₂₄ and Co(NO₃)₂, MoO₂(C₅H₇O₂)₂ and Co(C₅H₇O₂)₂ with chelating agent nitrilotriacetic acid (NTA) were studied for CoMo deposition in one impregnation step.

The textural parameters of the support and selected catalysts were determined by N₂ physisorption. The selected catalysts were characterized by x-ray diffraction, temperature programmed reduction (TPR) and O₂ chemisorption. The activity in HDS of 1-benzothiophene was determined to compare the prepared catalyst with industrial reference catalysts supported on conventional gamma-Al₂O₃. It was found that the highly dispersed and x-ray amorphous loadings of Mo linearly corresponded to specific surface area of the MgOs studied (about 330 m²g⁻¹ and 500 m²g⁻¹) and HDS activities. TPR measurement revealed that high Mo content in the Mo/MgO catalyst led to a decrease in the temperature of sulfides reduction and decrease in hydrogen consumption. The decrease of the reduction temperature is well related to the increase in the catalytic activity. In contrast, the decrease in hydrogen consumption indicated a decrease of sulfur edge sites, which may be in agreement with the high loadings of Mo but it is contradicted to the high HDS activities observed. Neither the hydrogen consumption nor the O₂ uptake, as a measure of the sulfide dispersion, explained the HDS activity trends. Furthermore, the depositions of Co resulted in 13-46 fold promotion of the activity of Mo/MgO catalysts. This promotion, however, was highly sensitive to the method of Co deposition and the MgO type. The most active catalysts were prepared by i) deposition of Co onto oxidic Mo catalyst prepared from MoO₃/methanol slurry or ii) deposition of Co onto presulfided Mo catalyst prepared from MoO₂(C₅H₇O₂)₂/methanol solution and iii) by co-impregnation from MoO₂(C₅H₇O₂)₂, Co(C₅H₇O₂)₂ and NTA solution of freshly calcined and dechlorinated MgO support with surface area of about 330 m² g⁻¹.

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