

Characterization of SiO₂ deposition on Ni/Al₂O₃ and MoO₃/Al₂O₃ catalysts

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Introduction

The modification of catalyst structures can be very important for achieving high activities, selectivities, and stabilities. Chemical vapor deposition (CVD) is one method that can be used for this purpose [1-3]. Fine control of the pore-opening of Ni/Al₂O₃ for the selective chemisorption of H₂ (2.9 Å) and the exclusion of larger molecules (N₂-3.6 Å, NH₃-3.6 Å, and CO-3.8 Å) was demonstrated in this work by depositing SiO₂ on the external surface of Ni/Al₂O₃ in a fluidized bed reactor. N₂ physisorption, H₂ and CO chemisorption, and NH₃ TPD were used to characterize the catalysts to investigate the effect of deposition time and temperature. The CVD technique was also applied to MoO₃/Al₂O₃ catalysts to study the mechanism, microstructure, and thickness of the SiO₂ deposition using solid state ²⁹Si NMR, ToF-SIMS, and ICP-MS. The activity of the coated Ni/Al₂O₃ catalysts for *n*-octane cracking was tested to see the effect of amount of SiO₂ deposition on acidity and reactivity.

Materials and Methods

The Ni/Al₂O₃ (17% Ni loading) and MoO₃/Al₂O₃ (10% Mo loading) catalysts were prepared by wet impregnation using Ni(NO₃)₂·6H₂O and (NH₄)₆Mo₇O₂₄·4H₂O respectively as precursors. SiO₂ was deposited on the catalysts using the hydrolysis of tetramethoxysilane (TMOS, 1-1.75%) with steam (10-14%) in a fluidized bed reactor at atmospheric pressure using N₂ as a carrier gas. The cracking of *n*-octane was performed in a fixed bed reactor at 400°C and atmospheric pressure.

Results and Discussion

The BET surface areas and the pore volumes of the Ni/Al₂O₃ and MoO₃/Al₂O₃ catalysts decreased as the deposition time increased. For the Ni/Al₂O₃ catalyst coated for 2.5 hours (0.31 g SiO₂ per g of sample), CO uptake reduced significantly while H₂ uptake remained constant, as shown in Figure 1. This result was an indication that the Ni sites were still accessible to H₂ while CO was excluded. Similarly the NH₃ uptake diminished to near zero for a sample coated for 3 hours (0.37 g SiO₂ per g of sample). The reduction in acidity was ascribed to the covering of acid sites on the external surface by the SiO₂ coating and reduced penetration into the pores by NH₃ because of the reduced size of the pore-openings.

Figure 2 shows the conversion of *n*-octane as it changes with SiO₂ deposition time during *n*-octane hydrocracking on Ni/Al₂O₃. The catalyst coated for 30 minutes showed the maximum conversion towards *n*-octane cracking, while the catalysts coated for 1.5 hours or longer showed no reactivity due to decreased acidity and narrowing of pores for *n*-octane penetration.

The ²⁹Si NMR of the coated MoO₃/Al₂O₃ catalysts suggested that the coating contained at least two layers of Si after 30 minutes of coating. ToF-SIMS results also suggested a thin layer of SiO₂ (2-3 monolayers), or an uneven distribution of SiO₂ on the surface which is due to the rough surface topology of the particles. Both positive and negative ToF-SIMS spectra revealed the presence of SiO_xH (x=1,2,3) and C_mH_n (m,n=1,2,3, etc) fragments which indicated that silanols and methoxy species are produced during the hydrolysis of TMOS. The mechanism of SiO₂ deposition was proposed to be first the adsorption of -Si-OCH₃ species on the substrate, followed by hydrolysis to form silanol and methanol, and the condensation of the silanol to form the Si-O-Si network.

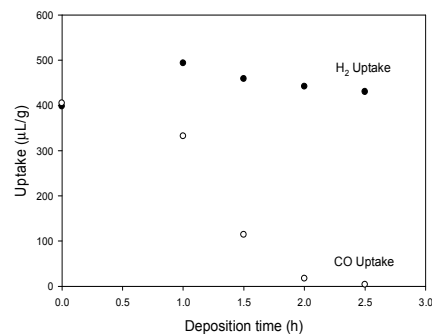


Figure 1. Change in H₂ (●) and CO (○) uptakes on Ni/Al₂O₃ with deposition time at a deposition temperature of 350°C

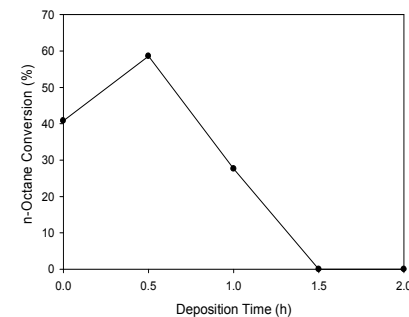


Figure 2. Change of *n*-octane conversion as a function of SiO₂ deposition time on Ni/Al₂O₃ during hydrocracking of *n*-octane at 400°C and atmospheric pressure

Significance

Proper characterization of the SiO₂ deposition helps to understand its structure and formation so that the technique can be better applied to the synthesis of novel catalysts to improve their activities, selectivities, and stabilities.

References

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