

Effect of Mn Promoter on Sulfated ZrO₂ Studied by IR Spectroscopy

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Introduction

Addition of Mn increases the activity of sulfated zirconia ("SZ") for *n*-butane isomerization [1] by 2-3 orders of magnitude [2]. To clarify the role of the promoter, SZ and Mn-promoted SZ ("MnSZ") and their interaction with H₂ and *n*-C₄H₁₀ were investigated by IR spectroscopy.

Experimental

SZ was prepared by calcining hydrous sulfated zirconia (SZH, MEL Chemicals) in flowing air at 823 K for 3 h. MnSZ (2 wt% Mn) was obtained through incipient wetness impregnation of SZH with Mn(NO₃)₂ aq. solution and calcination at 923 K for 3 h. Samples were pressed (2 s, 10 MPa), sieved (0.5-1.0 mm), and activated in vacuum at 723 K. Spectra were recorded with a Nicolet "Impact 410" FTIR spectrometer and a home-made diffuse reflectance attachment.

Results and Conclusions

The spectra of the activated samples were characterized by OH and SO vibrations and were similar with respect to the band positions. H₂ adsorption at 77 K produced bands at 4047 (SZ) and 4059 (MnSZ) cm⁻¹, indicating no significant difference in the Lewis acid strength. Heating to 473 K in H₂ (≈ 65 hPa) did not affect SZ, but the spectrum of MnSZ showed a new OH stretching band at ≈3580 cm⁻¹, a decrease of the bands belonging to sulfate vibrations, and formation of water on the surface. After contact with *n*-C₄H₁₀ (≈ 15 hPa) at 373 K, SZ was largely unaffected except for slight changes (shifts) in the OH region. At 573 K the sulfate bands shrank, and vibrations of olefinic CH and water were observed. MnSZ showed a significant intensity increase in the OH region already after interaction with *n*-C₄H₁₀ at 373 K. Additionally, a slight decrease of the sulfate bands and formation of water were detected. Promotion of sulfated zirconia by Mn thus modifies the reactivity of the sulfate groups, facilitating their easier interaction with reducing agents.

1. Hino, M., Kobayashi, S., and Arata, K., *J. Am. Chem. Soc.* **101**, 6439 (1979).
2. Lange, F.C., Cheung, T.-K., and Gates, B.C., *Catal. Lett.* **41**, 95 (1996).