



WO₃ monolayer loaded on ZrO₂: Property–activity relationship in *n*-butane isomerization evidenced by hydrogen adsorption and IR studies

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ABSTRACT

The property–activity relationship of WO₃ supported on ZrO₂ (WZ) was evaluated in *n*-butane isomerization for a series of catalysts with WO₃ loading ranging from 5 to 20 wt% on ZrO₂. The catalysts were prepared by incipient-wetness impregnation of Zr(OH)₄ with an aqueous solution of (NH₄)₆[H₂W₁₂O₄₀·*n*H₂O], followed by drying and calcination at 1093 K. The introduction of WO₃ continuously increased the tetragonal phase of ZrO₂, WO₃ surface density and coverage. The specific surface area and total pore volume passed through a maximum of WO₃ loading at 13 wt%; this loading corresponds to 5.9 WO₃/nm² and is near the theoretical monolayer-dispersed limit of WO₃ on ZrO₂. The IR results indicate that the presence of WO₃ eroded the absorbance bands at 3738 and 3650 cm^{−1} corresponding to bibridged and tribridged hydroxyl groups up to near the monolayer-dispersed limit of WO₃. A new broad and weak band appeared, centered at 2930 cm^{−1}, indicating the presence of bulk crystalline WO₃ for WO₃ coverage exceeding the theoretical monolayer-dispersion limit. In addition to the band at 2930 cm^{−1}, two W=O stretching bands were observed at about 1021 and 1014 cm^{−1} for all WZ catalysts, confirming the existence of W=O connected to coordinative unsaturated (cus) Zr⁴⁺ through O and to the other W through O, respectively. Pyridine adsorbed IR and NH₃-TPD revealed that the presence of WO₃ modified the nature and concentration of acidic sites. The highest acidity was observed with 13 wt% loading WO₃. The decrease in the intensity of peaks due to increasing WO₃ loading was much higher on Lewis acid sites than on Brønsted acid sites. Hydrogen adsorption isotherms and the IR results for hydrogen adsorption on preadsorbed pyridine were used to evaluate the formation of active protonic acid sites from molecular hydrogen. The catalyst with 13 wt% WO₃ loading showed the maximum hydrogen uptake capacity and formation of protonic acid sites. These results show a direct correlation with the activity of WZ in *n*-butane isomerization at 573 K in which 13 wt% WO₃ loading on ZrO₂ yielded the highest amount of isobutane. It is suggested that the presence of strong Lewis acid sites on monolayer-dispersed WO₃ facilitates the formation of protonic acid sites from hydrogen in the gas phase which act as active sites in *n*-butane isomerization. The presence of permanent Brønsted acid sites could not be directly associated with activity. In fact, no isomerization activity was observed in the absence of hydrogen.

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1. Introduction

Zirconia-based solid acid catalysts such as SO₄^{2−}–ZrO₂ (SZ), MoO₃–ZrO₂ (MZ) and WO₃–ZrO₂ (WZ) catalysts have been explored widely due to their potential for replacing halide-type solid acids and zeolite for linear alkane isomerization [1–7]. Skeletal isomerization over solid acid catalysts is normally carried out in the presence of hydrogen. Without hydrogen, catalytic activity decreases rapidly with the reaction time due to the formation

of coke deposits and/or the lack of active sites for isomerization. Our research group has studied the effects of hydrogen on the catalytic activities of SZ, MZ and WZ catalysts for acid-catalyzed reactions [8–10]. Our results suggest that protonic acid sites are generated from molecular hydrogen and act as catalytically active sites, not only for the skeletal isomerization of alkanes, but also for acid-catalyzed reactions such as cumene cracking and toluene disproportionation. On the basis of pyridine adsorbed IR, hydrogen adsorbed ESR and quantitative hydrogen adsorption studies, we have proposed the concept of “molecular hydrogen-originated protonic acid sites” that involves the generation of protonic acid sites on the surface of solid acid materials from molecular hydrogen [9–13]. Hydrogen molecules are dissociatively adsorbed on specific

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