

***n*-Butane Isomerization Catalyzed by Sulfated Zirconia Supported on Silica and γ -Alumina**

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Summary

Sulfated zirconia (SZ) was supported on silica and γ -alumina via incipient wetness impregnation of $\text{Zr}(\text{SO}_4)_2$ aqueous solutions followed by calcination at 923 K. The catalysts were characterized by means of thermal analysis, XRD, EXAFS, SEM/EDX, and DR-UV/Vis spectroscopy. Different manners of interaction of zirconia with silica and alumina have been observed; however, these differences have only been minorly reflected in the catalytic tests of *n*-butane isomerization at 378 K.

Introduction

Addition of small quantities of a second metal oxide component to sulfated zirconia can enhance the catalytic activity of the material for *n*-butane isomerization by 1 to 2 orders of magnitude. Oxides of Mn, Fe, [1] and more recently Al [2] have been observed to increase isomerization activity. These additional components can modify the geometric structure of the SZ catalyst, viz. the tetragonal zirconia fraction in the catalysts is increased with the addition of Fe and/or Mn [3]; or surface acidity of the SZ can be changed, e.g., there is a significantly larger number of moderate acid sites with the addition of Al [2]. In the present work, a novel approach is taken to understand the interaction between zirconia and a second oxide component, i.e., small amounts of sulfated zirconia are added to a chosen support material, silica or γ -alumina. To our knowledge, this methodology to disperse SZ catalysts onto support materials is not well demonstrated in the literature, with perhaps the exceptions of the preparation of zirconia films on silicon wafers [4] and of functionalizing M41S-type ordered mesoporous silica with zirconia components [5].

Experimental Section

Amorphous silica (Fluka Kieselgel 500) and γ -alumina (ALON) were calcined at 723 K for 4 h before the active component SZ was added. Dispersion of SZ on the supports was by incipient wetness impregnation of $\text{Zr}(\text{SO}_4)_2$ aqueous solutions with subsequent calcination at 923 K. Calculated amounts of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Alfa Aesar, 99%) were dissolved in 10.0 g of water acidified with 0.4 g 98% H_2SO_4 , and the

solutions were added drop-wise to 5.0 g of each of the supports in a time course of 6 h, achieving samples with 10, 20, and 50 wt% ZrO₂. Tests of catalytic activity were carried out at 378 K under atmospheric pressure in a flow type fixed-bed reactor with catalysts containing 200 mg ZrO₂ (activated at 723 K for 90 min) in a 30 cm³/min total flow of 1 vol% *n*-butane in N₂.

Results and Discussion

With loadings of up to 20 wt% ZrO₂, SZ catalyst can be dispersed onto either silica or γ -alumina supports; however, the manner of dispersion on the different support materials is quite different. Diffraction peaks of tetragonal ZrO₂ are observable in the XRD patterns of calcined SZ/SiO₂ samples, indicating a low degree of dispersion, thus a weak interaction between SZ and silica. In DR-UV/Vis spectra, the lowering of the band gap energy due to dispersion, in comparison to that of bulk sulfated ZrO₂, is not significant. SEM/EDX reveals an uneven distribution of zirconium species over silica surfaces. By contrast, the interaction between SZ and γ -alumina is much stronger. SZ is more highly dispersed on alumina surfaces, with no peaks of crystalline ZrO₂ detected by XRD. A lowering of the ZrO₂ band gap energy by ca. 1.5 eV is observable by DR-UV/Vis spectroscopy. Scanning electron microscopy shows images of finely distributed Zr on Al₂O₃ surfaces. Analysis of TG/DSC data leads to the conclusion that calcined SZ/ γ -Al₂O₃ samples contain 7 times as much sulfur species as SZ/SiO₂ samples, if loaded with the same amount of Zr(SO₄)₂. Surprisingly, the two series of catalysts do not differ from each other significantly in their catalytic activity for *n*-butane isomerization at 378 K (Fig.1).

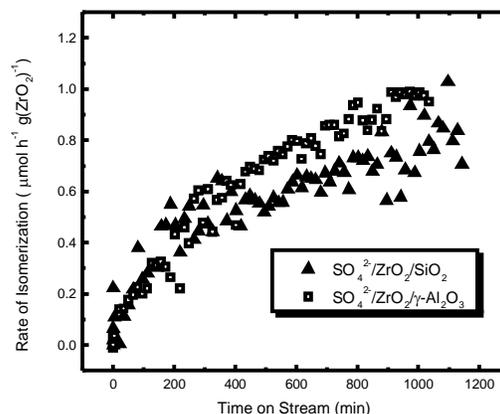


Fig. 1: Catalytic activity of supported SZ on silica and γ -alumina each with 10 wt% ZrO₂.

References

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