

Role of Bulk Phase in Sulfated Zirconia Catalysts

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Introduction

Sulfated zirconia, a catalyst in use for the low temperature skeletal isomerization of alkanes, has been investigated for more than two decades, but no convincing structure–activity relationship has evolved. A point in question is the role of the bulk phase of zirconia. First, only the tetragonal phase was considered to be active [1]; recently, the monoclinic phase, which is the room temperature stable modification, was reported to be similarly active [2]. Sulfated zirconia can be promoted by cations of Mn, Fe, Co, or Ni whose function is not yet understood [3]. The aim of this work was to study the nature and stability of the zirconia bulk structure and its influence on catalytic behavior, including deactivation and regeneration.

Results and Discussion

Three different types of SZ catalysts were investigated: (i) “SZ”, obtained through 3 h calcination at 823 K of sulfated hydrous zirconia (MEL Chemicals XZO 682/01), (ii) “MnSZ” and “FeSZ”, Mn- and Fe-promoted SZ, containing 0.5 to 5.0 wt% metal, obtained through incipient wetness impregnation of sulfated hydrous zirconia and subsequent calcination at 923 K [4], and (iii) “omSZ”, ordered mesoporous sulfated zirconia, obtained from zirconium *n*-propoxide, ammonium sulfate, and hexadecyl-tri-methyl-ammonium chloride at 373 K followed by calcination at 813 K [5].

Within the detection limits of XRD, only the tetragonal phase of zirconia was found in the calcined samples of SZ and of promoted SZ with promoter contents >1%. The promoters were in part incorporated into the bulk zirconia, as evidenced by a contraction of the unit cell (XRD), the presence of isolated Fe³⁺ and Mn²⁺ in a highly symmetric environment (EPR [6]), and, for MnSZ, the absence of Mn at the surface at low Mn contents (ISS).

The phase composition proved to be extremely sensitive to any kind of mechanical stress [7]. Grinding by hand in a mortar, milling in a vibrating mill, and pressing affected the phase composition in that monoclinic zirconia was formed. Depending on the treatment, the resulting monoclinic fraction was as much as 57 wt%. Two diffractograms of SZ powder and of an SZ wafer, which

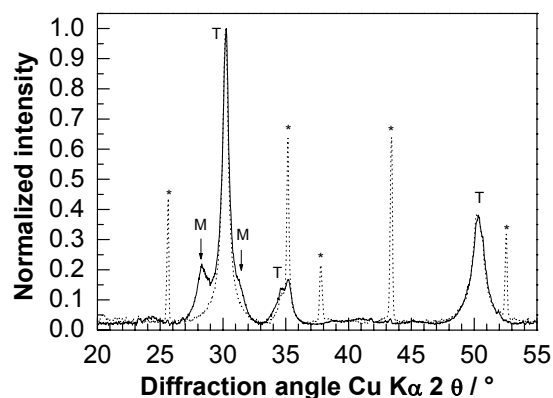


Figure 1: Diffractograms of SZ (dotted line, asterisks indicate internal standard corundum) and pressed SZ (solid line).

was prepared as for an IR experiment i.e. using 540 MPa of pressure, are shown in Figure 1. Arrows indicate the monoclinic phase, which contributed 33 wt%. Ground and milled SZ and MnSZ samples were also tested for their *n*-butane isomerization activity (fixed bed flow reactor, 0.5 g sample, activation at 723 K, 80 ml/min 1% *n*-butane in N₂ at atm. pressure, reaction at 323–378 K). Milled SZ and ground MnSZ (0.5%Mn) exhibited only 25–30% of the conversion attained with untreated sample.

Deactivation of SZ and omSZ was studied by in situ UV-vis spectroscopy [8]. Under the selected conditions (50 ml/min 5% *n*-butane, 1.2 g SZ at 378 K and 0.6 g omSZ at 453 K), SZ reached a maximum isomerization rate of 700 $\mu\text{mol g}^{-1} \text{h}^{-1}$ after 50 min and then deactivated rapidly, reaching a steady production of 100 $\mu\text{mol g}^{-1} \text{h}^{-1}$ at 150 min, omSZ also reached a maximum rate of 700 $\mu\text{mol g}^{-1} \text{h}^{-1}$ but only after 100 min and it deactivated slowly to 550 $\mu\text{mol g}^{-1} \text{h}^{-1}$ within 10 h. The spectra of SZ showed a band at 310 nm which developed during the period of high activity and then did not increase further. The spectra of omSZ showed a band at 285 nm which slowly grew in intensity throughout the observation span. Both these bands can be attributed to allylic cations [9], but the nature of the unsaturated species and/or the polarization through the underlying surface are different for the two catalysts.

A series of consecutive reactivation experiments were conducted with SZ, using 50% O₂ at 723 K and alternately a short (1 h) and a long (71–88 h) reactivation procedure. The short exposure to O₂ produced a more active and the long exposure a less active catalyst (Figure 2). The catalyst could be switched back and forth between these states. The different responses to O₂ on a scale of hours suggest solid state (bulk) reactions.

Our experiments show that the zirconia bulk plays a role in the promotion, deactivation, and reactivation of sulfated zirconia catalysts. The bulk phase is also metastable and transformations can occur during standard laboratory procedures.

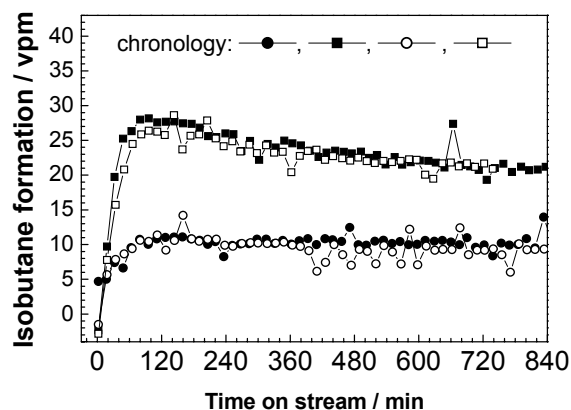


Figure 2: Isomerization activity of SZ at 338 K after regeneration in O₂ for 1 h (squares), and for 71–88 h (circles).

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