



Promoted Sulfated Zirconia: Modification of Zirconia Bulk through Incorporation of Fe and Mn Cations

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The activity of sulfated zirconia (SZ) for room temperature isomerization of *n*-butane is increased through the addition of Fe and Mn as promoters. The isomerization ability of promoted SZ suggests strongly acidic materials, but acidity measurements have not identified any sites sufficiently acidic to alone explain the activity [1], and it has been proposed that the promoters add a redox functionality to SZ [2]. We have addressed the role of Fe and Mn in promoted SZ using XRD, X-ray absorption spectroscopy (XAS), EPR, XPS and ion scattering spectroscopy (ISS) as well as catalysis measurements.

Fe-promoted and Mn-promoted sulfated zirconia were prepared from sulfated zirconium hydroxide (MEL Chemicals) and Fe(III) or Mn(II) nitrate through the incipient wetness method, followed by a 3 h calcination in flowing synthetic air at 923 K.

The room temperature stable phase of zirconia is monoclinic. Our XRD results show that addition of either Fe or Mn (0.5-2 wt%) to SZ not only stabilizes the tetragonal phase, but the stabilized phase has cell lattice constants smaller than those of pure tetragonal zirconia. These results indicate that the promoter ions are incorporated into the zirconia bulk (as with Ca or Y in "stabilized zirconia"), and are consistent with the literature [3]. XAS results of Mn K edge spectra of Mn-promoted SZ revealed two Mn species of different valence, one of which is tentatively assigned to Mn on Zr lattice sites. Additional evidence that promoter ions enter the zirconia lattice comes from EPR measurements which show one isolated Fe³⁺ species, in addition to at least one non-isolated species in 2 and 5 wt% Fe-promoted SZ. ISS and XRD data suggest that Mn is incorporated into the zirconia to a greater extent than Fe.

Although both Fe and Mn promote the alkane activation ability of SZ, their effect on activity for *n*-butane isomerization is not the same. In general, for the same promoter content, promotion with Mn alone gives higher maximum conversions, but more rapid deactivation, and promotion with Fe alone gives lower maximum conversions with slower deactivation (1% *n*-butane, 338 K, 1 atm, 9 h on stream). An additional difference between Fe and Mn promotion is observed from XAFS studies at the Mn and Fe K edges. These studies show that activation and reaction with *n*-butane of promoted SZ are accompanied by a reduction of Mn, whereas no change in Fe is observed.

Conclusions: Fe and Mn are incorporated into the zirconia lattice and modify its bulk properties. In Fe- or Mn-promoted SZ there are at least two promoter cation species present.

[1] V. Adeeva et al., *J. Catal.* **151** (1995) 364.

[2] K.T. Wan et al., *J. Catal.* **158** (1996) 311.

[3] J. Stöcker, *Ann. Chim.* **5** (1960) 1459.