

## Bulk Structural Characteristics of Sulfated Zirconia Catalysts

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### Introduction

Sulfated zirconia (SZ) is a catalyst for the structural isomerization of light hydrocarbons [1]. Promotion of SZ with Fe or Mn results in the incorporation of the promoter ions into the ZrO<sub>2</sub> bulk and in a catalyst that can isomerize *n*-butane at a rate two orders of magnitude greater than SZ [2]. Here we characterize the effect of this incorporation using XRD and XAS.

### Experimental

Sulfated zirconium hydroxide from MEL Chemicals was promoted by adding aqueous solutions of Mn(II) or Fe(III) nitrate (incipient wetness), to give 0.5 to 3.5 wt% promoter in the final catalyst. Precursor batches differing only in size (ca. 3.5, 12, or 26 g) were dried and then calcined at 650 °C. X-ray diffractometry was conducted in situ using Bragg-Brentano geometry and ex situ using both Bragg-Brentano and Debye-Scherrer geometry. Size and strain were determined by Williamson-Hall plots. XAS was performed at Hasylab.

### Results and Conclusion

Analysis of XRD measurements provided the tetragonal lattice parameters *a* and *c*, domain size, and the magnitude of strain in the ZrO<sub>2</sub> bulk. Promoted catalysts calcined in c.a. 26 gram batches show a higher maximum conversion (*n*-butane isomerization at 65 °C) than those calcined in smaller batches [3]. These large-batch catalysts have crystallite domains that are about 30 to 45% smaller and that are less strained than the domains of catalysts which were calcined in smaller batches and are less active. Promoted catalysts with a higher *c/a* ratio than that of SZ deactivate more slowly than those with *c/a* ratios lower than that of SZ, independent of whether the promoter is Fe or Mn. Zr K-edge XAS shows that the local (7 Å) structure around the zirconium atoms changes markedly with promoter type, concentration, and calcination atmosphere, and shows slight differences in the radial distribution function at about 3.3 Å for large-batch vs. smaller batch catalysts. These results are consistent with the idea that the ZrO<sub>2</sub> bulk structure influences the activity of promoted SZ catalysts.

[1] M.J. Hunter, DGMK-Conference "Chances for Innovative Processes at the Interface between Refining and Petrochemistry", Berlin, October 9-11, 2002.

[2] C.-Y. Hsu, C. Heimbuch, C.T. Armes, B.C. Gates, J. Chem. Soc., Chem. Comm. (1992), 1645.



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