

## Structure – Activity Relationships in Promoted Sulfated Zirconia

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### Introduction

Sulfated zirconia based catalysts are used for the isomerization of light hydrocarbons [1]. Their high potential for such reactions was identified more than 20 years ago [2]. However, despite extensive investigation there is not yet a consensus on the mechanism of their operation [3,4]. The activity of sulfated zirconia for *n*-butane isomerization increases 1-2 orders of magnitude upon addition of transition metal cation promoters (Fe, Mn, typically ca. 2 wt%) [5,6]. Recently, we have identified the amount of sample calcined as having a pronounced effect on the catalyst activity and reproducibility [7]. This usually not reported parameter and its influence on the resulting catalyst's activity allow us to synthesize and characterize catalysts from the same precursor, but with dramatically different activity. A clearer linkage of characterization and reaction characteristics may thus evolve due to a reduced number of "free parameters" in the preparation of the catalysts. Here we present X-ray diffraction (XRD) data of such a set of samples, analyzed using Pawley's method [8] for whole-powder-pattern fitting. This method, which does not reference a structural model, enables us to analyze the broad peaks of real catalysts in order to calculate precise cell parameters and to use the Williamson-Hall method to obtain size and strain information. In addition to ex situ XRD, in situ measurements were performed to determine the response of the catalyst structure to heat treatments under various gas atmospheres. Zr K-edge X-ray absorption spectroscopy (XAS) was used to gain complementary structural information.

### Experimental

Sulfated zirconium hydroxide from MEL Chemicals was promoted by adding aqueous solutions of Mn(II) or Fe(III) nitrate under vigorous stirring (incipient wetness method), followed by room temperature drying, to give 0.5 to 3.5 wt% promoter in the final catalyst. Thermal treatment (calcination) was carried out in quartz boats, sized for ca. 3.5, 12, and 26 g of precursor material, at 650°C under defined atmosphere. XRD experiments were performed using a STOE STADI-P-diffractometer applying Cu K $\alpha$  radiation. Ex situ diffractograms were recorded with high signal-to-noise ratios in De-

by-Scherrer geometry with a primary monochromator and a linear position sensitive detector with an internal resolution of  $0.01^\circ 2\theta$ . To analyze the data, Pawley's method was implemented, according to Toraya [9], as a new feature in the XAS/XRD data processing software WinXAS [10]. In situ diffractograms were recorded in Bragg-Brentano geometry with a secondary monochromator and a Bühler HDK S1 high temperature diffraction chamber mounted on the goniometer. XAS was performed at Hasylab, DESY, Hamburg. *n*-Butane isomerization was conducted at atmospheric pressure in a once-through plug-flow fixed bed reactor at 65 °C and products were quantified using on-line gas chromatography with FID.

## Results and discussion

Analysis of the ex situ XRD measurements reveals systematic differences between samples from the same precursor as a function of the amount calcined. The investigated parameters were the tetragonal lattice parameters *a* and *c*, the *c/a* ratio, the domain sizes, and the strain. The maximum activity (also a function of the amount calcined), the integrated conversion, and the rate of deactivation of the catalysts was linked to the structural parameters. Promoted catalysts with higher *c/a* ratio deactivated more slowly while those with lower *c/a* ratios exhibit rapid deactivation. Moreover, this link was independent of the type of promoter cation (Fe or Mn). In situ XRD measurements were used to monitor the bulk structure of the catalyst during treatment in atmospheres and at temperatures under which the catalyst is activated and can be reactivated. These results are presented in context with changes in the valence of the promoter ions under similar treatments. The correlations obtained from XRD measurements are compared to results from measurement of Zr K-edge X-ray absorption spectra that reflect the local structure of the zirconium atoms.

## References

- [1] M.J. Hunter, DGMK-Conference "Chances for Innovative Processes at the Interface between Refining and Petrochemistry", Berlin, October 9-11, 2002.
- [2] M. Hino, K. Arata, *J. Chem. Soc. Chem. Comm.* (1980), 851.
- [3] X. Song, Y. Sayari, *Catal. Rev. - Sci. Eng.* **38** (1996), 329.
- [4] K.T. Wan, C.B. Khouw, M.E. Davis, *J. Catal.* **158** (1996) 311.
- [5] C.-Y. Hsu, C. Heimbuch, C.T. Armes, B.C. Gates, *J. Chem. Soc., Chem. Comm.* (1992), 1645.
- [6] F.C. Lange, T.-K. Cheung, B.C. Gates, *Catal. Lett.* **41** (1996), 95.
- [7] A. Hahn, T. Ressler, R.E. Jentoft, F.C. Jentoft, *Chem. Comm.* (2001), 537.
- [8] G.S. Pawley, *J. Appl. Cryst.* **10** (1981), 357.
- [9] H. Toraya, *J. Appl. Cryst.* **19** (1986), 440.
- [10] T. Ressler, *J. Synchrotron Radiation* **5** (1998), 118.