

## Comparison of Tetragonal and Ordered Mesoporous Sulfated ZrO<sub>2</sub>: Alkane Isomerization Studied by In Situ DR UV-vis Spectroscopy

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### Introduction

The role of the ZrO<sub>2</sub> bulk structure in sulfated zirconia (SZ) catalysts is unclear. We compare SZ of tetragonal structure (tSZ) to ordered mesoporous SZ of MCM-41 structure (omSZ), focussing on performance and deactivation behavior in *n*-butane and *n*-pentane isomerization.

### Experimental

tSZ was obtained by calcination of a commercial precursor, omSZ in a procedure based on the description by Ciesla [1,2]. In situ DR-UV-vis-NIR spectra were recorded using a lambda 9 spectrometer (PerkinElmer) with integrating sphere and a fixed bed flow reactor [3]. Products of *n*-butane (5 kPa in He) and *n*-pentane (1 kPa) isomerization were analyzed by on-line GC.

### Results and Discussion

tSZ exhibited a higher maximum activity than omSZ; to obtain comparable rates, conditions were varied. For *n*-butane isomerization catalyzed by tSZ at 378 K, the conversion increased over 50 min and then declined in the next 100 min to a steady state. Despite a higher reaction temperature of 453 K, omSZ, which passed through a 100 min induction period, deactivated only slowly. Both catalysts produced propane and pentanes as side products, suggesting a similar mode of operation. During the deactivation phase, which stretched over 100 min for tSZ and over more than 900 min for omSZ, bands developed in the UV-vis spectra. A band at 310 nm was detected for tSZ and assigned to allylic cations; for omSZ, the band was positioned at 285 nm. In the reaction with *n*-pentane, the materials produced more isobutane than isopentane within the observation span of 15 h. Both catalysts deactivated rapidly while bands at 330 nm (tSZ, 298 K) and 285 nm with a shoulder at ≈330 nm (omSZ, 323 K) formed. Unsaturated species are formed on both materials but they are either differently polarized by the surface or differently structured, indicating an influence of the nature of the ZrO<sub>2</sub> structure.

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2. X. Yang, F.C. Jentoft, R.E. Jentoft, F. Girgsdies, T. Ressler, *Catal. Lett.* **81** (2002) 25.
3. M. Thiede, J. Melsheimer, *Rev. Sci. Inst.* **73** (2002) 394.