

Deactivation and Regeneration of Mn-Promoted Sulfated Zirconia Alkane Isomerization Catalysts: An In-Situ Spectroscopic Study

B.S. Klose, R.E. Jentoft, T. Ressler, A. Trunschke, R. Schlögl, F.C. Jentoft
*Fritz Haber Institute of the Max Planck Society, Department of Inorganic Chemistry
Faradayweg 4-6, 14195 Berlin, Germany; email: jentoft@fhi-berlin.mpg.de*

The activity of sulfated zirconia (SZ) for alkane isomerization can be improved by doping with transition metals (Mn, Fe) in cationic form [1]. Unpromoted and promoted catalysts deactivate rapidly, and deposits are formed on the surface of SZ [2]. It has been proposed that the reaction is initiated not by acid catalysis but by oxidative dehydrogenation, implying that either sulfate [3] or promoter species are reduced. To evaluate these theories, to gain understanding of the alkane activation, and to identify causes of deactivation and procedures for reactivation we performed in situ IR (sulfate), UV-vis (Mn valence, "coke") and X-ray absorption spectroscopy (Mn valence).

Mn-promoted SZ catalysts with up to 2 wt% Mn were produced from sulfated zirconium hydroxide (MEL Chemicals XZO 682/01) via incipient wetness impregnation and subsequent calcination at 923 K [4]. In situ DRIFTS was conducted using a Graseby-Specac "Selector" attachment with environmental chamber placed in a Bruker ifs 66 spectrometer. In situ UV-vis spectra were acquired with an FHI-design in situ cell and a PE lambda 9. Product analysis for IR and UV-vis experiments was performed by on-line GC. XAFS spectra were taken in fluorescence mode at the Hamburg Synchrotron Radiation Laboratory beamline E4 using a fixed-bed reactor with on-line MS analysis. All experiments were done in flow with activation and regeneration at 703 – 773 K in inert or oxidative atmosphere and reaction at 323 – 338 K at 1 kPa *n*-butane.

XAS data yielded an initial (= calcined catalyst) average Mn valence of 2.65, and UV-vis spectra exhibited bands at 570 and 675 nm. IR spectra taken during activation showed mainly dehydration; while the XAS results indicated some reduction of Mn even in oxidative atmosphere. Under the selected conditions the catalyst underwent an induction period followed by a short peak activity and deactivation over 1 – 6 h. The Mn valence remained unchanged or decreased at a constant rate through all stages, hence activity is not directly linked to Mn stoichiometric reduction. The DRIFT spectra showed an overall decrease in intensity and more water on the surface, only one new band at 1305 cm⁻¹ could be discerned. The S=O stretching vibration shifted from 1400 to 1375 cm⁻¹. The initial IR spectrum and the catalyst activity could be completely recovered by reactivation in 100% oxygen, suggesting that there are no irreversible changes to the catalyst such as sulfur loss. The Mn valence was somewhat higher after activation or reactivation in oxidative atmosphere than after treatment in inert gas, and there was a correlation between the initial valence and the maximum isomerization rate. Attempts to regenerate in inert gas resulted in bands at 1530 and 1465 cm⁻¹, which are explained by further reaction of surface deposits formed during reaction to more highly unsaturated species. The S=O band was restored but the catalyst was inactive.

The data indicate that hydrocarbon species block active sites but do not affect the sulfate, which then can constitute only part of the site. The role of Mn will be discussed.

References:

- [1] F.C. Lange, T.-K. Cheung, B.C. Gates, *Catal. Lett.* 41 (1996) 95.
- [2] R. Ahmad, J. Melsheimer, F.C. Jentoft, R. Schlögl, *J. Catal.* 218 (2003) 365.
- [3] C.R. Vera, C.L. Pieck, K. Shimizu, C.A. Querini, J.M. Parera, *J. Catal.* 187 (1999) 39.
- [4] A. Hahn, T. Ressler, R.E. Jentoft, F.C. Jentoft, *Chem. Comm.* (2001) 537.