

In Situ X-Ray Absorption Spectroscopy of Manganese Promoted Sulfated Zirconia Catalysts

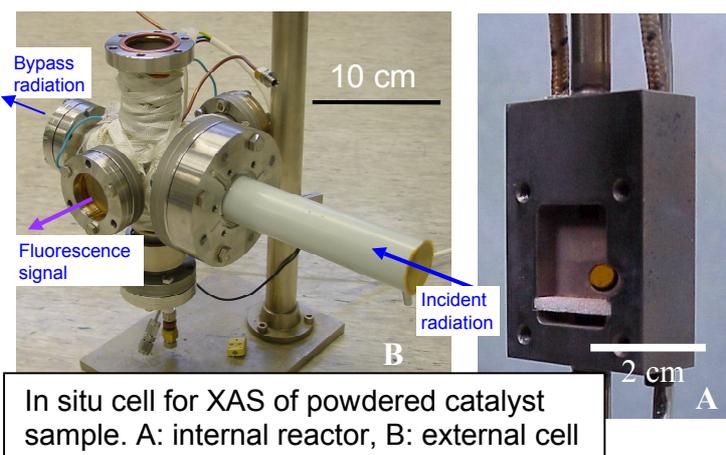
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Abstract:

Sulfated Zirconia (SZ) is an active catalyst for low temperature skeletal isomerization of light hydrocarbons [1,2]. Addition of transition metal cations (Mn, Fe) to SZ can result in an isomerization catalyst with a maximum activity two orders of magnitude greater than that of SZ [3]. The mechanism of the promotion effect is not yet understood. The literature suggests that Fe ions initiate the isomerization in a stoichiometric reaction with the alkane leading to reduction of Fe^{3+} [4,5]. We have characterized a 2 wt% Mn promoted catalyst using in situ X-ray absorption spectroscopy of the Mn K edge during activation of the catalyst (heating in He or 50% O_2 to 723 K) and during the isomerization reaction (1% *n*-butane at 333 K).

Promoted SZ when pressed into a wafer shows a reduced activity. It was therefore necessary to build an in situ cell that could be used to measure spectra of a powder catalyst sample. The cell consists of an internal powder bed reactor (heatable to 773 K) in which the catalyst is supported on a glass frit, Fig. A. The internal reactor is enclosed in a He filled temperature controlled outer cell to ensure that the window to the inner cell, and the catalyst contacts, are at the set temperature, Fig. B. The spectra are measured in fluorescence mode. An energy calibration is obtained from a portion of the beam which bypasses the catalyst bed.



Mn in SZ was found to have an average valence of 2.7. The average Mn valence decreased during activation (10 K/min to 723 K in either He or 50% O_2). When activated in He, the Mn valence decreases to 2.5 and remains constant during reaction. When activated in 50% O_2 the Mn valence decreases to about 2.6 and shows a decrease during the reaction to about 2.5. The Mn valence does seem to indicate a catalyst with high maximum activity; however, the decrease in Mn valence correlates neither with the reaction rate nor to an observed induction period in the reaction.



MAX-PLANCK-GESELLSCHAFT

GDCh Workshop
Hamburg 16. – 17- 09. 2002



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It seems clear that Mn cations do not participate directly in stoichiometric redox reactions during catalytic isomerization of *n*-butane. Mn promoter cations are incorporated into the zirconia bulk, and the changes observed in the oxidation state during activation may indicate further changes in the zirconia bulk. The role of the Mn may be its ability to modify the zirconia bulk, tuning the surface activity.

- [1] M. Hino, S. Kobayashi, and K. Arata, *J. Am. Chem. Soc.*, 101 (1979) 6439.
- [2] X. Song and A. Sayari, *Catal. Rev.*, 38(3) (1996) 329.
- [3] C. -J. Hsu, C. R. Heimbuch, C.T. Armes, and B.C. Gates, *Chem. Comm.*, (1992) 1645.
- [4] K.T. Wan, C.B. Khouw, M.E. Davis, *J. Catal.*, 158 (1996) 311.
- [5] C. Morterra, G. Cerrato, S. Di Ciero, M. Signoretto, A. Minesso, F. Pinna, G. Strukul, *Catal. Lett.*, 49 (1997) 25.