



**Surface properties of Fe-promoted sulfated zirconia catalysts:
Probe molecule adsorption studied by microcalorimetry & IR spectroscopy**



Sabine Wrabetz, Jutta Kröhnert, Alexander Hahn, Friederike C. Jentoft, Robert Schlögl

Fritz Haber Institute of the Max Planck Society, Department of Inorganic Chemistry, Faradayweg 4-6,
D-14195 Berlin, Germany, wrabetz@fhi-berlin.mpg.de

Sulfated zirconia (SZ) is a catalyst for the industrially important low temperature isomerization of light alkanes, e.g. of *n*-butane at 373 K [1]. The activity of SZ is increased by 1–2 orders of magnitude through addition of Mn or Fe cations [2]. Sulfur content, zirconia phase composition, and surface area have been found to affect catalyst performance [3]; and these properties depend strongly on the preparation procedure. However, differently active catalysts can be generated by using one precursor material and just varying the batch size for calcination [4]. Such samples exhibit many identical properties, so those that differ are most likely responsible for differences in activity. Here, we probe sites on such a family of samples with *neo*-pentane, which is closely related to *n*-butane but will only adsorb and not react.

Catalysts “FeSZ”, containing 2 wt% Fe, were calcined at 923 K in batches of 3, 10, and 20 g. The respective maximum isomerization rates relate as 1: 2.3: 8.6. A SETARAM MS70 Calvet calorimeter and a Nicolet Protégé 466 FTIR spectrometer were used. The sample cells that were placed in the calorimeter or the IR beam were part of calibrated volumetric systems. *Neo*-pentane was adsorbed at 313 K (calorimetry) or 308 K (FTIR).

Adsorption isotherms for differently active FeSZ samples indicate no significant variation in the number of sites interacting with *neo*-pentane molecules. Differential heats of *neo*-pentane adsorption at coverages >10 $\mu\text{mol/g}$ reveal that the majority of sites produce 55–60 kJ/mol. Differential heats at low coverages <10 $\mu\text{mol/g}$ show that only a minority of sites interact more strongly with 60–80 kJ/mol. In comparison *iso*-butane (product of test reaction) detects the same number of adsorption sites as *neo*-pentane, but the interaction is ≈ 20 kJ/mol weaker. In IR spectra, the intensity of a band is proportional to the change of the dipole moment during vibration and may reflect the polarization of a molecule through adsorption. Polarization is the beginning of a catalytic transformation. We are testing a new hypothesis, namely whether intensities, or more specifically, extinction coefficients of certain vibrations are suitable to predict catalytic activity. The extinction coefficient can be determined when the adsorbed amount is known. The extinction coefficient of *neo*-pentane in the CH-stretching region (ca. 3050–2650 cm^{-1}) in the gas phase was determined to be 160 km/mol. After adsorption on FeSZ samples it increased by up to one order of magnitude, demonstrating pronounced polarization of *neo*-pentane in the adsorbed state. The calorimetry results suggest that the adsorbed state on differently FeSZ is equivalent (same differential heats). A trend of the extinction coefficients of the different stretching and bending vibrations for *neo*-pentane adsorbed on the series of three catalysts was so far difficult to discern. It remains to be resolved whether an IR extinction coefficient presents a quantity that is more sensitive to subtle differences in the adsorbed state than a heat.

The active sites on SZ catalysts so far remain unidentified. If equilibrium adsorption methods fail to distinguish differently active catalysts, the dynamic properties of the catalyst may be the key, and relevant information can only be retrieved under catalytic conditions.

1. M. Hino, K. Arata, *J. Am. Chem. Soc.*, **101** (1979) 6439.
2. C.-Y. Hsu, C. R. Heimbuch, C. T. Armes, B. C. Gates, *Chem. Comm.*, 1645 (1992).
3. X. Song, A. Sayari, *Cat. Rev. Sci. Eng.*, **38**, 329 (1996).
4. A. Hahn, T. Ressler, R. E. Jentoft, F. C. Jentoft, *Chem. Comm.*, **537** (2001).
5. L. C. Jozefowicz, H. G. Karge, E. N. Coker, *J. Phys. Chem.*, **98** (1994) 8053.