

Active Site Characterization of Sulfated Zirconia Catalysts for *n*-Butane Isomerization

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Sulfated zirconia is an active catalyst for the low temperature isomerization of *n*-butane which is of great industrial importance [1]. The activation of *n*-butane on the catalyst surface as well as the function of surface active centres and their influence on the reaction path is still under consideration.

Our well-defined zirconia samples [2] were investigated using microcalorimetry, temporal analysis of products (TAP) and in situ IR-spectroscopy. With the combination of these methods we intend to characterize the surface sites of zirconia during the interaction with different probe molecules.

Sample Preparation

Zirconia precursors were produced from zirconyl nitrate solutions by aging the precipitate at 298 K for 1 h (precursor for SZ-1) or 373 K for 24 h (SZ-2), respectively. After drying, the samples were sulfated with ammonium sulfate (20 mol% nominal content) and subsequently calcined for 3 h at 873 K. An industrial catalyst, calcined MEL XZO 1077, was used for comparison.

Results and Discussion

SZ-1 and SZ-2 were characterized by standard techniques [2]. Interestingly, we found that the catalytic activities of these two samples do not scale with their BET surface areas (Table 1).

Table 1: BET-surface areas [m^2/g], sulfate content (wt%) and *n*-butane isomerization rates at 373 K [$\text{mol}/(\text{g}\cdot\text{sec})$]

	BET	SO ₄ ²⁻	Isomerization rate
SZ-1	102	9.2	$7 \cdot 10^{-8}$
SZ-2	152	8.9	$8 \cdot 10^{-10}$

Almost identical sulfate content at different surface area suggests different sulfate coverages; and evidence is given by TAP measurements using CO₂ as a probe molecule (Fig. 1): Only the curves obtained for SZ-2 indicate strong interaction with CO₂ and thus the presence of basic sites, which origin from sulfate-free zirconia surface areas. IR spectra are consistent with slightly different sulfate structures on the two materials.

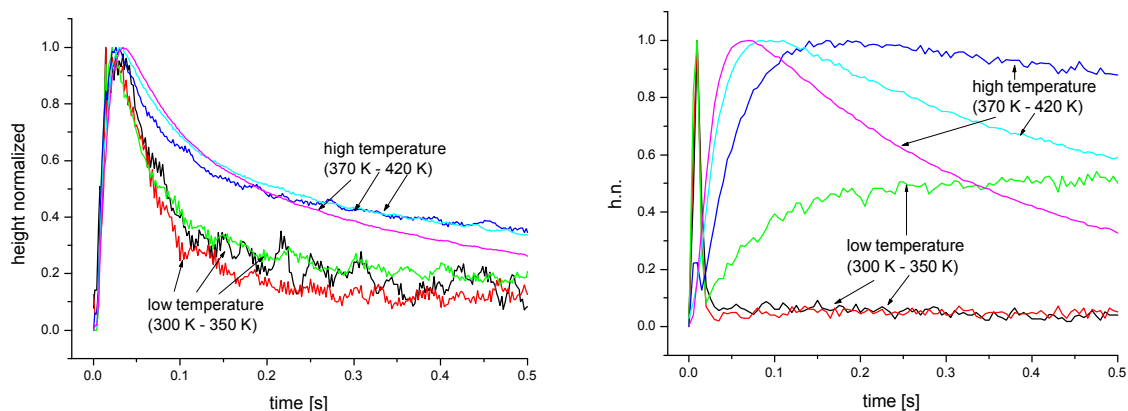


Fig. 1: Height normalized response curves (amu 44) for pulses of CO₂ on SZ-1 (left) and SZ-2 (right).

TAP measurements with *n*-butane and iso-butane also showed slight differences in the adsorption behavior.

Because sulfated zirconia catalysts typically first pass through an induction period (Fig. 2 top) and deactivate rather quickly after they reach maximum activity, we have investigated samples at different stages of activity. Isobutane adsorption isotherms (Fig. 2 bottom) show a decrease of sites with time on stream, consistent with sites blocked by irreversibly adsorbed species. TAP experiments, mimicking flow-like exposure to *n*-butane through thousands of pulses, reveal a change in residence time with increasing pulse number.

Our data show: (i) only a fraction of the sulfate on the surface generates active sites, and (ii) the catalyst surface changes during the reaction, making studies at different stages of catalyst activity, preferably in situ experiments, compulsory.

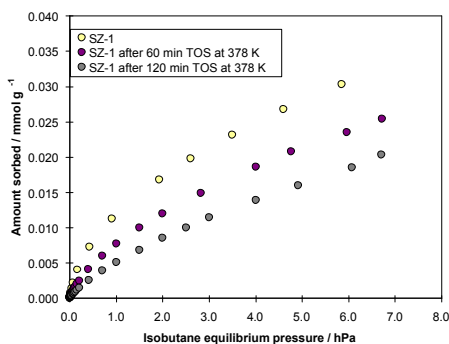
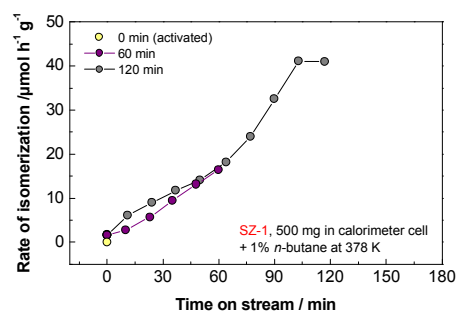


Fig. 2: Isobutane adsorption isotherms recorded after exposure of SZ-1 to *n*-butane for different time periods and subsequent evacuation at 378 K. Adsorption at 313 K. First isotherm after activation only (723 K).

[1] M. Hino, S. Kobayashi, K. Arata, *J. Am. Chem. Soc.* **101** (1979) 6439.

[2] M. Standke, C. Bretkopf, H. Papp, S. Wrabetz, B.S. Klose, X. Yang, R.E. Jentoft, F.C. Jentoft, X. Li, L.J. Simon, J.A. Lercher: Proceedings of the DGMK-Conference "Chances for Innovative Processes at the Interface between Refining and Petrochemistry", Berlin, October 9-11, 2002, ISBN 3-931850-98-6, pp. 23-30.