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A Comparison of Two Special Sulfated Zirconia Samples: Characterization & Interaction with Alkanes



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Sulfated zirconia is an active catalyst for the industrially important low temperature isomerization of alkanes [1]. So far, it has neither been possible to reveal the nature of the active sites nor the complete reaction mechanism. We succeeded in preparing two sulfated zirconia samples whose catalytic activity does not scale with BET surface area (Fig.1). The samples were investigated using XRD, SEM, Zr K edge XAS, TPR, TPD, microcalorimetry, TAP, and in situ UV/Vis & IR spectroscopies.

Sample Preparation

Two different hydrous 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.

Results and Discussion

The BET surface areas were determined to be 102 m²/g for SZ-1 and 152 m²/g for SZ-2. Both materials feature mesopores of about 3.8 nm diameter. SEM images showed SZ-2 to consist of finely dispersed particles while SZ-1 formed 10-15 μm sized chunks. XRD indicated the crystalline fraction to be mainly tetragonal ZrO₂ in both cases but the diffractogram of SZ-2 exhibited broader peaks.

SZ-1 and SZ-2 were active for *n*-butane isomerization at 378

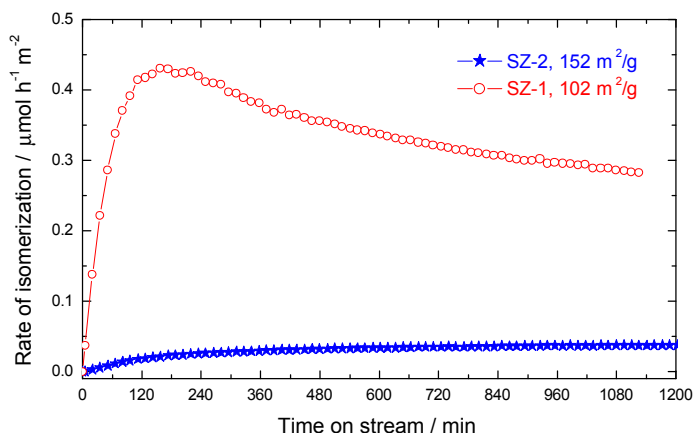


Fig. 1: *n*-Butane isomerization rate vs. time on stream. Conditions: 500 mg catalyst, activated at 723 K in N₂; feed 30 ml/min of 1% *n*-butane in N₂, T = 378 K.

K (Fig. 1), and both catalysts underwent an induction period of about 2 h with steadily increasing conversion. SZ-1 was more active than SZ-2 but deactivated rapidly and did not reach a steady state within 20 h. SZ-2 was a remarkably stable catalyst giving a constant conversion over 45 h.

Ammonia-TPD profiles extended from 400 - 800 K with a maximum at about 425 K, but these profiles were too ill-defined to identify different sites. SZ-1 adsorbed 0.48 mmol NH₃/g vs. 0.52 mmol NH₃/g adsorbed by SZ-2; these data could not be related to the catalytic activities. The strong base ammonia thus appears to be an unselective probe for distinguishing isomerization sites on these catalysts.

Alkane adsorption isotherms were consistent with the catalytic data rather than with the BET surface areas (Fig. 2) in that the catalytically more active sample SZ-1 provided more sites for chemisorption of propane or isobutane than SZ-2. At the same equilibrium pressure, both samples adsorbed more isobutane than propane. Differential heats of adsorption of propane and isobutane reached about 50 - 60 kJ/mol for the majority of sites on both samples. TPD of *n*-butane revealed the desorption of traces of unsaturated hydrocarbons from SZ-1 but not from SZ-2, suggesting that the two materials differ not only in the number but also in the nature of adsorption sites.

A model consistent with the data obtained so far would include the presence of one type of site on SZ-2 producing a stable activity, and of two types of sites on SZ-1, one type equivalent to the sites on SZ-2 producing a "base" activity and one type a highly active species producing the peak activity but also deactivating rapidly.

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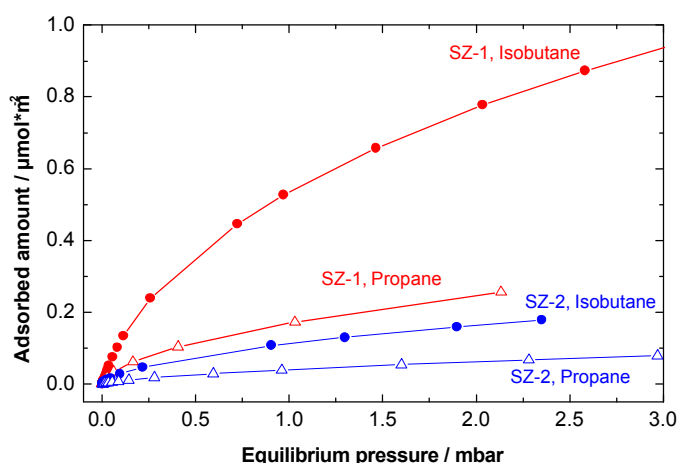


Fig. 2: Alkane adsorption at 313 K. Activation at 723 K in vacuum.