

Quasi *in-situ* Adsorptive Microcalorimetric Characterization of Sulfated Zirconia Catalyst for *n*-Butane Isomerization with *n*-Butane and Isobutane as Probe Molecules

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Sulfated zirconia (SZ with 0.94 mmol/g sulfur and 100 m²/g) is an active catalyst for the industrially important low temperature (373 K) isomerization of light alkanes, e.g. of *n*-butane [1]. The catalytic activity exhibits a multicomponent profile along time-on-stream (TOS) including an activation period and a maximum followed by rapid deactivation. This observation suggests a continuous change of the catalyst under reaction conditions, especially, of the sites that gain activity during the induction period. It has been found that a freshly prepared catalyst shows some characteristics that are far from those of the catalyst during reaction. Also it is known that probe molecules such as NH₃ and pyridine, which are often used for catalyst characterization by adsorptive microcalorimetry, interact with the active sites much stronger than the reactant. It is hence compulsory to do characterization *in-situ* using probe molecules with the same characteristics as the reactant. Therefore, we developed a quasi *in-situ* adsorptive microcalorimetric method in order to characterize the active sites on SZ. The calorimeter cell was used as a fixed bed flow reactor, in which the catalytic reaction of *n*-butane isomerisation was carried out (0.5 g SZ pellets, 378 K, 1 kPa *n*-butane in N₂). The feed was introduced through a capillary. Conversion was monitored on-line by GC. The reaction was stopped after various TOS, the cell was evacuated at 378 K, and placed in a SETARAM MS 70 calorimeter equipped with a volumetric system that allows dosages of < 0.01 µmol [2]. Adsorption of *n*- or isobutane was performed at 313 K [3].

The *n*- and isobutane adsorption isotherms of the SZ catalyst at different TOS indicate that the number of sites interacting with educt- (*n*-butane) and product (isobutane) molecules decreases with TOS, especially, during the induction period. Only a modified and not the simple Langmuir model fits these adsorption isotherms [4]. The order of adsorption decreases with the increasing catalytic activity, e.g. *n*-butane adsorption from 1.7 (TOS = 0) to 1.1 (TOS = 120 min). This indicates a more complicated, maybe activated adsorption process. Differential heats of butanes adsorption at coverages > 2 µmol/g show that the majority of sites produce 40 – 50 kJ/mol. These stable sites are probably related to the steady state activity of SZ beyond the activity maximum. Differential heats at < 20 µmol/g show that only a minority (< 2% of sulfur species) of sites change their character during the induction period. It seems that only these sites determine the induction process.

The state of highest activity is characterized by a strong interaction of *n*-butane with the active sites (75 kJ/mol at < 2 µmol/g). However, the weak interaction of isobutane (50 kJ/mol at < 2 µmol/g) indicates an increasing easiness of product-desorption from the surface sites. The adsorbed amount of *n*-butane and isobutane is comparable (ca. 20 µmol/g at 6 mbar).

In the state of highest activity the catalyst reacted with *n*-butane in the calorimeter cell (additional heat evolution, gas phase products).

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