



## Site Changes on Sulfated Zirconia during *n*-Butane Isomerization: Quasi-In-Situ Adsorption Calorimetry Study with Butanes as Probes

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### Introduction

Sulfated zirconia (SZ) changes its performance for *n*-butane isomerization considerably with time on stream (TOS). To probe the relevant sites on active SZ we interrupted the reaction at different stages (induction period, maximum conversion), removed weakly adsorbed species, and measured adsorption isotherms and differential heats of adsorption ( $q_{\text{diff}}$ ) of butanes.

### Experimental

The calorimeter cell was used as a fixed bed flow reactor (0.5 g SZ, 378 K, 1 kPa *n*-butane in N<sub>2</sub>); the feed was introduced through a capillary. Conversion was monitored by on-line GC. The reaction was stopped after various TOS, the cell was evacuated at 378 K, and placed in a SETARAM MS 70 calorimeter [1]. Adsorption of *n*- or isobutane was performed at 313 K.

### Results and Discussion

The isotherms at TOS = 0 could not be fit with a 1<sup>st</sup> order Langmuir model, indicating a more complicated, maybe activated adsorption process. The differential heats for *n*- and isobutane adsorption on the unreacted catalyst were similar. The adsorption isotherms for *n*- and isobutane indicate a decrease of the number of sites for these molecules during the induction period and with further increasing TOS. Throughout the catalytic reaction, the shape of the isotherms changed and the apparent reaction orders decreased approaching 1. At the state of maximum activity, SZ adsorbed similar amounts of *n*-butane and isobutane (ca. 20  $\mu\text{mol/g}$  at 6 hPa), and the majority of these sites (coverages > 2  $\mu\text{mol/g}$ ) produced  $q_{\text{diff}} \approx 40\text{-}50$  kJ/mol for both adsorptives. At coverages < 2  $\mu\text{mol/g}$ ,  $q_{\text{diff}}$  for *n*-butane was as high as 85 kJ/mol, while for isobutane it never exceeded 50 kJ/mol.

Quasi-in-situ adsorption microcalorimetry with butanes as probe molecules revealed that only a small number of sites on SZ changes with the performance in *n*-butane isomerization.

1. L.C. Jozefowicz, H.G. Karge, E.N. Coker, *J. Phys. Chem.* **98** (1994) 8053.