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## Interaction of Zirconia Catalysts with Alkanes and CO: Investigation by Microcalorimetry and IR Spectroscopy



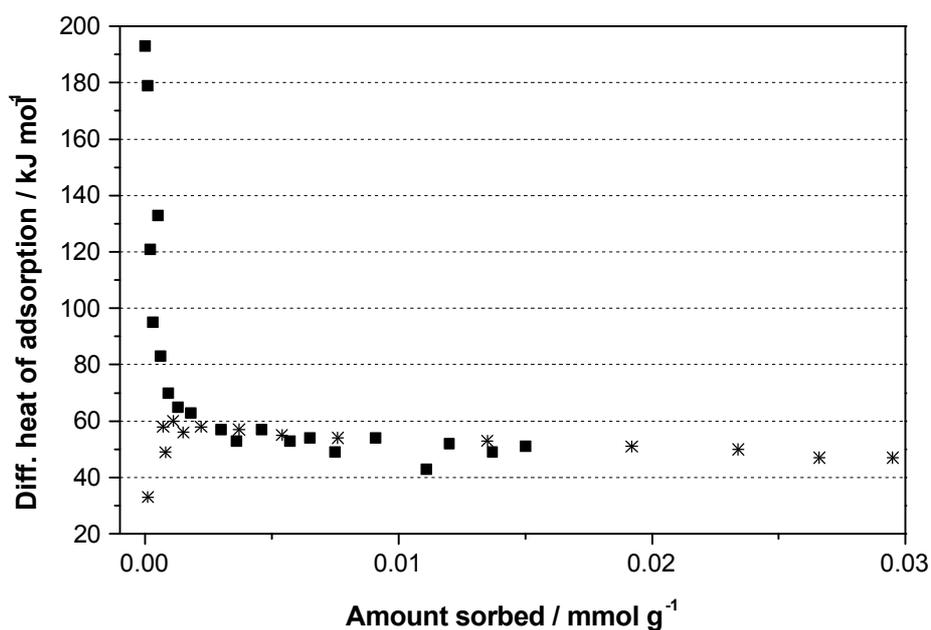
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Sulfated zirconia (SZ) is active for the isomerization of *n*-butane to isobutane at room temperature [1]. The activity was first ascribed to strongly (super) acidic sites, however, it was not possible to identify such sites on the surface of SZ [2]. The addition of cations of Fe and/or Mn increases the activity of SZ for *n*-butane isomerization by 1-2 orders of magnitude [3,4]. Particularly with respect to Fe and Mn it was suggested that functionalities other than acidic sites contribute to the reactivity of sulfated zirconia materials [5].

The investigation of acidic sites on sulfated zirconia with standard probe molecules such as pyridine, ammonia, or substituted benzenes is problematic because the sulfate may be displaced or -upon heating for thermal desorption spectroscopy- the sulfate and/or the probe may decompose [6,7]. Large or strongly basic probes can thus be considered unsuitable for sulfated zirconia. We used propane and isobutane, i.e. molecules that are chemically closely related to the reactant *n*-butane, and CO, a weak base, as probe molecules.

Zirconium hydroxide and sulfated zirconium hydroxide were obtained from MEL Chemicals. The promoters, Fe and Mn, were added in the form of solutions of their nitrates according to the incipient wetness method [4]. Unpromoted samples were calcined at 823 K, promoted samples at 923 K. The batch size for calcination which has been demonstrated to have a significant effect on the activity of the obtained catalysts [8] was varied in some cases (10-25 g). IR spectroscopy was performed with a PE System 2000 spectrometer in transmission using self-supporting wafers, and CO was adsorbed at 77 K. Differential heats of adsorption were measured with modified SETARAM Calvet calorimeters, and the alkanes were adsorbed at 313 K. Samples were activated at 723 K in vacuum for IR and microcalorimetry experiments.



**Figure 1:** Differential heats of adsorption of propane (solid squares) and isobutane (stars) vs. coverage. Sample: 2wt.% Fe-promoted sulfated zirconia. T = 313 K.

*Microcalorimetry:* The majority of chemisorption sites for alkanes on SZ and promoted SZ was nearly equivalent, with heats of chemisorption of 40 - 50 kJ/mol for propane and 50 - 60 kJ/mol for isobutane. At very low coverages, i.e. below 2  $\mu\text{mol/g}$ , the evolved heat was coverage-dependent. Using propane as probe, a normal profile was obtained, i.e. the heat decreased with increasing coverage, starting at more than 100 kJ/mol. Using isobutane as probe, an unusual profile was obtained, i.e. the heat increased with increasing coverage, starting at 30 kJ/mol. The heats of interaction with propane and isobutane measured at these low coverages increased with the age (= time stored on shelf) of the sample, and the heats also changed when the alkanes were removed by evacuation and the samples were subjected to a second adsorption cycle.

*IR spectroscopy:* The CO adsorption on Mn-promoted SZ produced a number of bands in the carbonyl stretching region and shifts of the bands in the OH and SO stretching region. The S=O band at  $1390\text{ cm}^{-1}$  shifted continuously with increasing CO pressure to  $1364\text{ cm}^{-1}$  at 5 mbar CO. Up to a partial pressure of about 0.25 mbar CO, two major bands were observed in the carbonyl region: at  $2188\text{ cm}^{-1}$ , this band is assigned to the adsorption on Lewis sites; and at  $2169\text{ cm}^{-1}$ , this band builds up as the band at  $3655\text{ cm}^{-1}$  shifts to  $3530\text{ cm}^{-1}$  and is thus assigned to the adsorption of CO on the Brønsted sites producing the band at  $3655\text{ cm}^{-1}$ . With further increasing pressure, bands at  $2144\text{ cm}^{-1}$  and  $2135\text{ cm}^{-1}$  appeared. Only when performing a second activation of the sample, an OH band at  $3767\text{ cm}^{-1}$  was clearly visible and this OH group also interacted with CO. In comparison with literature data [9] for SZ, the much more active Mn-promoted SZ does not display strongly acidic Lewis sites (at  $2204\text{ cm}^{-1}$  for SZ, [9]), suggesting these sites may be irrelevant for reactivity.

The results of the CO adsorption suggest the presence of a number of different Lewis and Brønsted sites, but the microcalorimetry results suggest that the majority of sites are similar as far as the interaction with alkanes is concerned. Only molecules that are chemically related to alkanes may thus be suitable to probe the active sites on these catalysts.

#### *References:*

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