



Role of Non-Sulfated Zirconia Surface for Alkane Adsorption



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Introduction

Catalysts based on sulfated zirconia materials have been implemented into industrial low temperature alkane isomerization units [1]. Zirconia itself is inactive for this type of reaction and becomes active only through addition of sulfate. Optimization of the sulfate content has been performed empirically [2], but it is e.g. not known whether complete coverage of the zirconia surface with sulfate is desirable or whether sites on the zirconia itself play a role in the reaction scheme. The goal of this work was to develop a method to detect free zirconia surface, to quantify its extent depending on the preparation procedure, and to assess the role of such sulfate-free areas of zirconia for the interaction with alkanes.

Experimental

The sulfate content and coverage were varied by different methods, namely (i) the amount of sulfate added in the sulfation process [3], (ii) the temperature for calcination of sulfated zirconium hydroxide (MEL Chemicals) or zirconium sulfate, (iii) removal of sulfate by washing, and (iv) SO₃ treatment [4]. CO₂ is tested as a probe for free zirconia surface, using TPD, TAP and IR spectroscopy. Common sites for CO₂ and alkanes were identified by comparison with calorimetric results and by consecutive interaction with both probes followed by TPD, TAP and in situ DRIFTS.

Results

In TPD experiments CO₂ is retained on the surface of pure zirconia up to 823 K (Fig. 1), indicating formation of stable carbonates with basic sites. Sulfated samples adsorb little or no CO₂; specifically in the presence of enough sulfate and calcination

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at a moderate temperature of 773 K all zirconia sites are found covered by sulfate. After exposure of such a sample to *n*-butane at 773 K and subsequent evacuation, a small amount of CO₂ can be adsorbed. Volatile compounds such as H₂S form upon contact with butane already at 573 K [5], providing sulfate-free patches for CO₂ adsorption. On samples partially desulfated via water-washing, DRIFTS spectra show an increased amount of CO₂ linearly adsorbed on Lewis acid sites. Sulfate, known to increase the strength of Lewis acid sites on zirconia, also blocks Lewis sites.

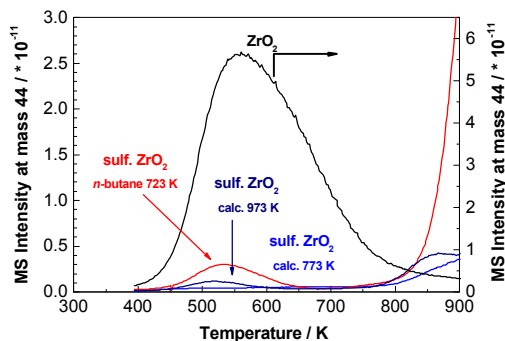


Figure 1: CO₂ TPD

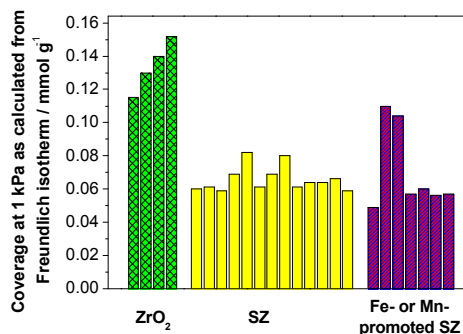


Figure 2: Isobutane monolayer coverage.

The importance of the sulfate coverage becomes evident from analysis of isobutane adsorption isotherms (Fig. 2). On a number of samples higher coverages of isobutane at equal pressures are consistently observed on non-sulfated materials (despite generally lower surface areas). IR spectra show *n*-butane and *n*-pentane interacting with OH groups of sulfated zirconia, but also with OH groups of pure zirconia and those of partially desulfated (by water washing) inactive sulfated zirconia.

Conclusions

CO₂ is identified as a sensitive probe for Lewis acid and basic sites on “bare” patches of zirconia in a sulfated material. Alkanes adsorb on surface OH groups, and surprisingly, more adsorption sites are provided by pure than by sulfated zirconia.

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