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Structural and Active Site Characterization of Sulfated Zirconia Catalysts for Light Alkane Isomerization

Abstract

Two different sulfated zirconia catalysts were produced through precipitation from zirconyl nitrate solutions, followed by aging of the precipitate either at 298 K for 1 h (SZ-1) or 373 K for 24 h (SZ-2). After drying, the samples were sulfated with ammonium sulfate and calcined for 3 h at 873 K. SZ-1 had a smaller surface area ($90 \text{ m}^2 \text{ g}^{-1}$) than SZ-2 ($140 \text{ m}^2 \text{ g}^{-1}$) but displayed a one order of magnitude higher maximum *n*-butane isomerization rate (373–423 K, 1–5 kPa *n*-butane at 101.3 kPa total pressure). Both materials consisted predominantly of tetragonal ZrO_2 , contained 9 wt% of sulfate, and adsorbed about $0.5 \text{ mmol g}^{-1} \text{ NH}_3$. Measurements of adsorption isotherms and differential heats for propane and *iso*-butane at 313 K reveal a larger number of adsorption sites on SZ-1 than on SZ-2, extrapolated to 1 kPa, 42 vs. 20 $\mu\text{mol g}^{-1}$ (propane) and 120 vs. 44 $\mu\text{mol g}^{-1}$ (*iso*-butane). At coverages $> 2 \mu\text{mol g}^{-1}$ the heats were similar for both samples with both probes and decreased from 60 to 40 kJ mol^{-1} . Temporal analysis of products measurements indicated shorter residence times for *n*-butane than for *iso*-butane, and SZ-1 retained both of these molecules longer than SZ-2. The activation energy for *n*-butane desorption was 45 kJ mol^{-1} for both samples. Interaction with pulses of CO_2 suggested that non-sulfated, basic ZrO_2 surface is exposed on SZ-2, consistent with the larger surface area at the same sulfate content as SZ-1. The results suggest that only a fraction of the sulfate groups participates in adsorption and that product desorption may be of importance.

Keywords: sulfated zirconia, alkane isomerization, temporal analysis of products, heat of adsorption, isotherm, propane, butane, carbon dioxide

Introduction

Sulfated zirconia (SZ) is catalytically active for the industrially important *n*-butane isomerization at temperatures as low as 373 K [1] and is an interesting catalyst for a number of other reactions [2]. The material has thus been investigated extensively in the past two decades [2,3]. Although the influence of certain preparation parameters, e.g. the calcinations conditions, on the catalytic activity, sulfur content, surface area,

and phase composition has been asserted [2-4] no convincing structure-activity relationship has been established.

In the present work we compare two different SZ materials that have an interesting combination of properties. The work is aimed at complete structural characterization and identification of surface sites. In order to probe the sites, the following molecules are employed: (i) "classical" probes such as NH_3 and CO_2 , (ii) reaction participants and model compounds that are closely related to the reactants such as *n*-butane, *iso*-butane, and propane. The interaction with the probe molecules is investigated over a wide pressure and coverage range by the combination of transient and equilibrium methods.

Experimental

Two different types of sulfated zirconia were prepared through precipitation from zirconyl nitrate solution by addition of NH_4OH to a final pH of 8.4. The precipitate was aged in the mother liquor either for 1 h at 298 K (series 1) or for 24 h at 373 K (series 2). The precipitates were washed and dried for 24 h at 393 K, giving the precursors Z-1 and Z-2, respectively, which were sulfated by suspending them in a solution of ammonium sulfate (theoretical Zr:S ratio = 4). The sulfated materials were dried for 20 h at 373 K, and then calcined for 3 h at 873 K, giving the samples SZ-1 and SZ-2. Catalytic tests were run in fixed bed tubular plug flow reactors. The samples were activated at 673 - 723 K and then cooled to the reaction temperature of 378 - 423 K, all in inert gas. The feed was a mixture of 1.0 - 5.0 vol.% *n*-butane in inert gas at atmospheric pressure. The effluent stream was analyzed by on-line gas chromatography with flame ionization detection.

Surface area measurements were performed with an ASAP-2000, scanning electron microscopy with a Hitachi S-4000-FEG / EDAX DX4 using 5 kV acceleration voltage and secondary electron mode. For X-ray diffraction, the powders were mixed 1:1 with an internal standard ($\alpha\text{-Al}_2\text{O}_3$) and then measured in Debye-Scherrer geometry on a STOE STADI-P diffractometer using $\text{Cu K}\alpha$ radiation. The sulfur content was determined by ion chromatography. X-ray absorption spectra of the Zr K edge were recorded at beamline X-1 at HASYLAB. Diffuse reflectance Fourier transform IR spectroscopy (DRIFTS) was carried out in a commercial diffuse reflectance unit (Graseby-Specac) placed in a Bruker ifs 66 spectrometer. For temperature-

programmed desorption (TPD) of NH_3 , the catalyst was exposed to $300 \mu\text{l NH}_3$ at 373 K. Then the sample was heated with 10 K min^{-1} and desorbing NH_3 was detected by MS ($m/q=15$).

Temporal analysis of products (TAP) was conducted in a TAP-2 system [5] in the temperature range 323-523 K. Probe molecules were *n*-butane, *iso*-butane, and CO_2 ; 100 mg of sample were exposed to pulses of 10^{13} - 10^{17} molecules.

Adsorption isotherms and differential heats of adsorption, q_{diff} , were obtained using modified SETARAM Calvet calorimeters in combination with a volumetric system [6,7]. Samples were activated in vacuum at 723 K and transferred to the calorimeter. Adsorption of propane and *iso*-butane was performed at 313 K.

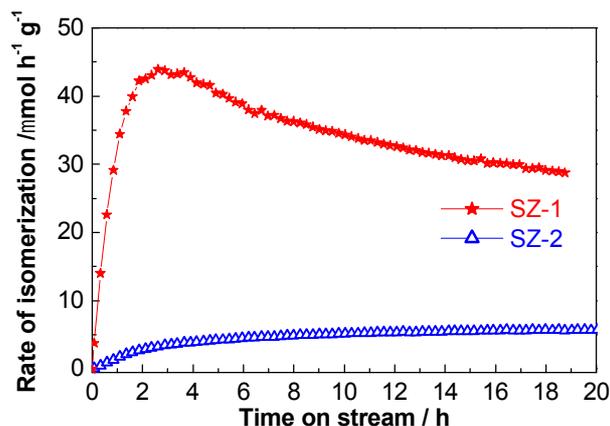


Fig. 1: *n*-Butane isomerization rate vs. time on stream. Conditions: 500 mg catalyst, activation in $50 \text{ ml min}^{-1} \text{ N}_2$ at 723 K for 1.5 h; reaction at 378 K, 1 kPa *n*-butane partial pressure, total flow 30 ml min^{-1} .

Catalytic tests: *n*-butane isomerization

The results of the catalytic tests are shown Fig. 1. The two catalysts show entirely different profiles with time on stream. SZ-1 displays a 2 h increase of the isomerization rate, followed by gradual deactivation. SZ-2 is almost one order of magnitude less active for the test reaction and did not deactivate within the observation span of 20 h. At 10 h on stream, the selectivity towards *iso*-butane was 97.5% for SZ-1 at a conversion of 2.19%, and 98.0% for SZ-2 at a conversion of 0.33%.

Catalyst characterization

SEM images (Fig. 2) exhibited slightly larger

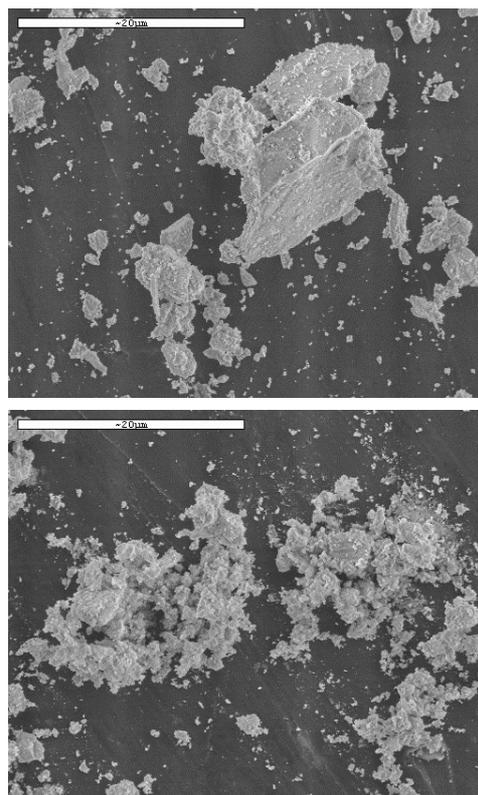


Fig. 2: SEM images of SZ-1 (top) and SZ-2 (bottom); scale bar is 20 μm .

particles for SZ-1 (5-20 μm) than for SZ-2 (1-5 μm). X-ray diffractograms showed SZ-1 and SZ-2 to consist predominantly of tetragonal ZrO_2 , but SZ-2 exhibited smaller crystalline domains than SZ-1 (7.5 vs. 10 nm). This observation was confirmed by Zr K edge X-ray absorption spectra in comparison to those of well-crystallized tetragonal ZrO_2 (Y-stabilized). Interestingly, the Zr K edge spectra of the precursors Z-1 and Z-2 were nearly identical.

Table 1: Results of nitrogen sorption

Property / Sample	BET surface area m^2/g	Pore diameter nm	Pore volume cm^3/g
Z-1	49	6.3	0.12
Z-2	87	5.0	0.15
SZ-1	90	3.5	0.09
SZ-2	140	4.0	0.15

Data from nitrogen adsorption are summarized in the table above. The most striking results are the BET surface areas of the two catalysts. SZ-1, the much more active catalyst has with 90 m^2/g a significantly lower surface area than SZ-2 with 140 m^2/g . The activity difference thus cannot be explained by a surface area difference.

Given the fact that both catalysts have the same sulfate content, i.e. 9 wt%, and assuming that all sulfur is at the surface, the density of sulfate groups on the surface must be considerably different, which may lead to the formation of different sulfate structures.

The nature of the sulfate groups was investigated by DRIFTS, and spectra were taken during the activation process. Fig. 3 reflects the situation at 573 K. At this temperature, the position of the maximum of the S=O stretching vibration differed by 24 cm^{-1} for SZ-1 and SZ-2, indicating a different configuration of the sulfate groups. An additional important issue is the surface sulfate coverage because the unmodified

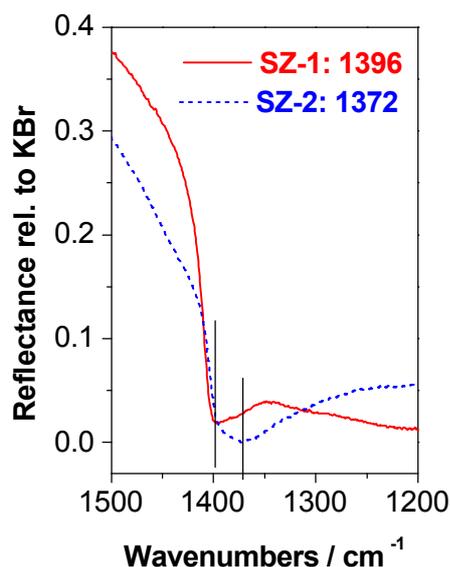


Fig. 3: DRIFT spectra of SZ-1 and SZ-2 after activation at 573 K in flowing N_2 , region of sulfur-oxygen double bond stretching vibrations.

zirconia provides basic sites of considerable strength. The coverage does not only depend on sulfate content and surface area, but also on the exposed facet planes and the sulfate coordination (mono-, bi-, tridentate) [8]. For a sulfate content of 9 wt% and the given surface areas, the coverage should in principle be complete.

NH₃-TPD (Fig. 4) did not reveal any significant differences between the two catalysts. The concentration of acid sites was determined to be 0.52 and 0.48 mmol g⁻¹ for SZ-1 and SZ-2, respectively, and it is not possible to derive an explanation for the catalytic activities from the profiles.

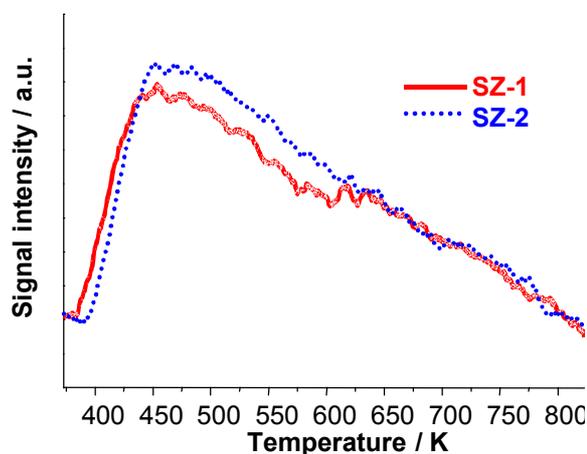


Fig. 4: NH₃-TPD for SZ-1 and SZ-2.

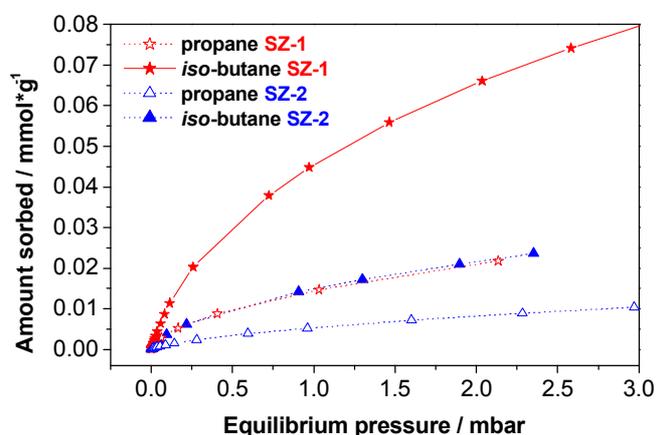


Fig. 5a: Adsorption isotherms for the adsorption of propane and *iso*-butane on SZ-1 and SZ-2 at 313 K.

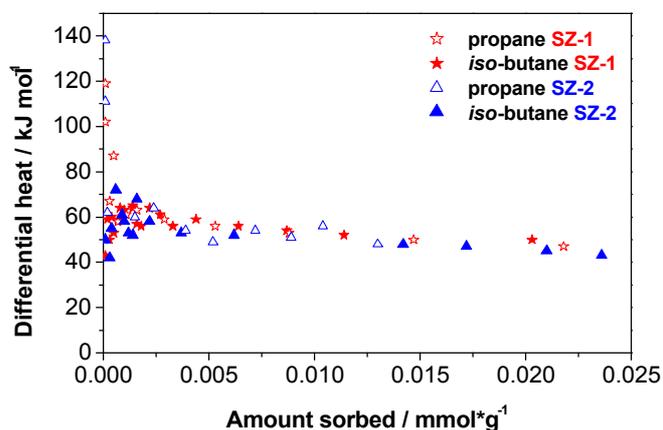


Fig. 5b: Differential heats for the adsorption of propane and *iso*-butane on SZ-1 and SZ-2 at 313 K.

Alkane adsorption: isotherms and heats of adsorption

Fig. 5a shows the isotherms for the adsorption of propane and *iso*-butane on SZ-1 and SZ-2. From these curves it becomes evident that the more active SZ-1 adsorbs much more propane or *iso*-butane than the less active SZ-2 at equal partial pressures. As opposed to the results of N₂ and NH₃ adsorption, these curves help explain the different catalytic activity, i.e. SZ-1 appears to provide more sites for the adsorption of small alkanes. The differential heats of adsorption (Fig. 5b) suggest that the majority of sites on the two

catalysts are similar. The isotherms can thus be fit with a modified Langmuir model and the coverage at the usual reactant partial pressure of 1 kPa can be estimated. On SZ-1, about 120 $\mu\text{mol g}^{-1}$ *iso*-butane and 42 $\mu\text{mol g}^{-1}$ propane would be adsorbed, on SZ-2 44 $\mu\text{mol g}^{-1}$ *iso*-butane and 20 $\mu\text{mol g}^{-1}$ propane. The sulfate content of 9 wt% corresponds to 938 μmol sulfate per g, it thus follows that only a fraction of the sulfate groups is involved. At coverages $< 2 \mu\text{mol g}^{-1}$, sites with different heats of adsorption are detected (Fig. 5b). Adsorption of *n*-butane reveals seemingly fewer sites for SZ-1 than for SZ-2, but fragmentation of *n*-butane has not yet been excluded; and if it occurred the measurement would produce a false result with fewer sites for the more reactive material.

Temporal Analysis of Products (TAP)

Table 2 summarizes the residence times for pulsing *n*-butane and *iso*-butane over precursor and catalyst samples.

Table 2. TAP-residence times in seconds for pulses of *n*-butane and *iso*-butane over Z-1, SZ-1, Z-2, SZ-2 calculated by using $m/q = 43$

	<i>n</i> -butane				<i>iso</i> -butane			
T [K]	Z-1	SZ-1	Z-2	SZ-2	Z-1	SZ-1	Z-2	SZ-2
323	0.552	0.652	-	-	0.624	0.584	0.643	0.608
373	0.524	0.500	0.517	0.523	0.495	0.464	0.510	0.519
398	0.423	0.439	0.434	0.443	0.406	0.385	0.412	0.421
423	0.314	0.347	0.329	0.347	0.298	0.274	0.304	0.322
458	0.197	0.254	0.251	0.244	0.202	0.185	0.220	0.218
473	0.149	0.187	0.180	0.173	0.148	0.140	0.165	0.161
523	-	0.133	-	0.121	-	0.105	-	0.119

The residence times decrease with increasing temperature. It is evident that pulses of *n*-butane and *iso*-butane onto the surfaces of precursors and catalysts result in different residence times indicating that the interaction of the probe molecules with the surfaces differs. For pulses of *n*-butane, the residence times for the catalysts samples are slightly higher than for the precursor samples showing the higher interaction of the probe molecule with the sulfated surface. This is also observable for pulses of *iso*-butane onto the pair Z-2/SZ-2. Interestingly the more active catalyst SZ-1 shows a decrease in residence time for *iso*-butane with respect to its precursor Z-1.

The interaction of *iso*-butane with the surface of zirconia is thus stronger in the absence of sulfate groups. At temperatures ≤ 423 K, the residence times for both alkanes are shorter in the case of SZ-1 than in the case of SZ-2. In general, all residence times also show a correlation to the BET surface areas of the samples: the higher the surface area, the higher the interaction time.

Fig. 6: Height normalized response curves for pulses of *n*-butane on SZ-1; temperature as parameter.

Based on the temperature dependent response curves (Fig. 6) it was also possible to create an activation plot [5] for the adsorption process of *n*-butane on the surfaces of SZ-1 and SZ-2. Both activation plots are very similar and result in an activation energy of 45 kJ mol^{-1} .

Another molecule was used to probe the surface of the zirconia catalysts. Unlike *n*-butane, CO_2 should only adsorb and desorb and not react. However, the pulse response curves do show a significantly different behavior for both catalyst samples (Fig. 7). Specifically, the residence times of CO_2 on SZ-2 are much longer compared to those on SZ-1. Due to the high noise at low temperatures it is not possible to quantify the difference without large error.

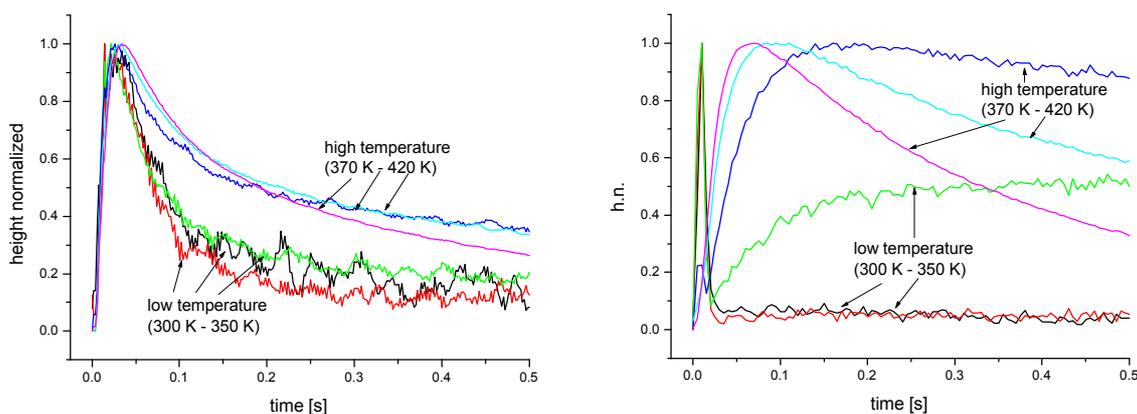


Fig. 7: Height normalized response curves (amu 44) for pulses of CO_2 on SZ-1 (left) and SZ-2 (right).

The area normalized response curves (not shown here) for SZ-2 have shapes typical of a reaction process. With increasing temperature CO_2 desorbs slowly from the surface ($T > 397$ K). For lower temperatures CO_2 is irreversibly adsorbed on the

surface. SZ-1 shows mainly the "normal" curve shape for adsorption and desorption. The change in the pulse shapes through surface reaction is much smaller for SZ-1 than for SZ-2. Our explanation for this different behavior is a different surface coverage with sulfate groups for SZ-1 and SZ-2. Because of the larger surface area of SZ-2, some non-sulfated surface may be exposed. ZrO_2 is strongly basic (Lewis basicity of oxide ions) so that CO_2 can react to form carbonates. These results are thus in good agreement with the results of textural characterization and DRIFTS presented above.

Summary

Two sulfated zirconia materials with catalytic activities (SZ-1 > SZ-2) different by an order of magnitude were prepared. The catalytic activities were not correlated to the surface areas (SZ-1: $90 \text{ m}^2 \text{ g}^{-1}$, SZ-2: $140 \text{ m}^2 \text{ g}^{-1}$). Sulfate content (9 wt%) and the number of acid sites as probed by NH_3 adsorption were similar for both materials ($\approx 0.5 \text{ mmol g}^{-1}$). Only the use of small alkanes and CO_2 as probes in TAP and calorimetric experiments in order to identify all types of sites revealed explanations for the catalytic properties. SZ-2, the less active material with the higher surface area is obviously not fully sulfate-covered because it interacts with CO_2 (presence of Lewis basic sites). SZ-1 adsorbs more hydrocarbon than SZ-2, and the estimated number of sites covered with alkanes at reaction pressures is small ($< 150 \text{ } \mu\text{mol g}^{-1}$) which means that only a fraction of the sulfate groups are involved. Results of *iso*-butane adsorption suggest that product adsorption and desorption play a role.

Acknowledgements

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