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Labile sulfates as key components in active sulfated zirconia for *n*-butane isomerization at low temperatures

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Abstract

A wide variety of sulfate species exists on sulfated zirconia and many of these species have been connected to the catalytic performance. Some of these groups show strong interactions with polar molecules, indicating that they may play a role for the catalytic properties. In order to differentiate between these groups and to explore the role of labile soluble sulfate for *n*-butane skeletal isomerization, active sulfated zirconia was washed with water. Water washing removed around 40% of the sulfate species and led to a catalyst inactive for the alkane isomerization. This indicates that the labile sulfate plays a key role for the catalysis. The water-soluble fraction of the sulfate exists as highly covalent sulfate species characterized by an S=O vibration between 1390 and 1410 cm^{-1} on the activated sulfated zirconia. Brønsted acid sites related to the sulfate groups are shown to be indispensable for activating *n*-butane, while Lewis acid sites do not directly participate in the alkane conversion catalysis.

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Keywords: Sulfated zirconia; Butane; Isomerization; Labile sulfate; Water washing

1. Introduction

Sulfated zirconia and other sulfated metal oxides have been studied for over two decades owing to their high catalytic activity for activation of short alkanes at low temperatures [1]. However, a general consensus on their surface chemical properties has not been reached. There are pronounced debates on the strength and type of acid sites, the state of the sulfate, and the influence of the zirconia support [1,2]. Because the strong acidity of sulfated zirconia is related to the introduction of sulfates on the zirconia surface, the state of the sulfate has been frequently explored.

Using IR spectroscopy to investigate sulfated zirconia, Yamaguchi [3] proposed that the sulfate species after hydration is similar to inorganic chelating bidentate species. Removal of water resulted in the formation of a sulfate resembling more organic sulfates with a stronger covalent character of the S=O double band. The model proposed by Arata and Hino [4] also involves a bidentate sulfate.

However, Lavalley and co-workers [5] proposed a structure model of sulfated zirconia with tridentate surface sulfate species containing just one S=O bond based on their IR results of ^{18}O exchange using $H_2{}^{18}O$ vapor at 450 °C. The results of Riemer et al. [6] also support the presence of tridentate surface sulfate species. However, these authors suggested that a HSO_4^- group was present at the surface, because an O–H stretching band at 3650 cm^{-1} was observed in the presence of sulfates, which was absent on the sulfate-free material. White et al. [7], in contrast, proposed a pentacoordinated sulfur in the active structure of sulfated zirconia.

Mono-dentate bisulfate species (HSO_4^-) are proposed in models independently by Kustov et al. [8] and Adeeva et al. [9]. The bisulfate OH group is hydrogen-bonded to one surface oxygen atom of zirconia. Bi-dentate bisulfate-like species were also affiliated with the formation of Brønsted acid sites in the active structure models of Clearfield et al. [10], Morterra et al. [11], and Lavalley and co-workers [5]. The model proposed by Riemer et al. [6] in-

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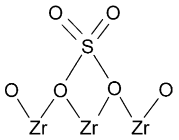
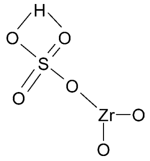
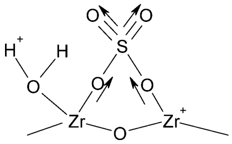
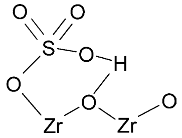
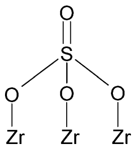
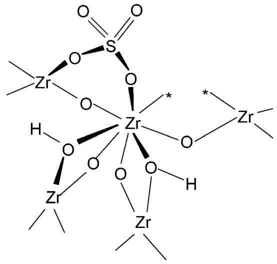
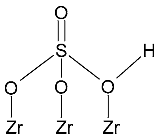
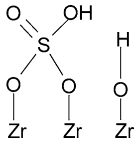
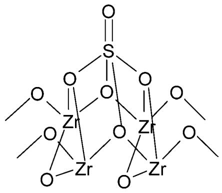
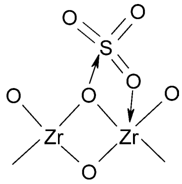
Table 1
Sulfated zirconia surface models proposed in previous literature

Authors	Surface model	Authors	Surface model
Yamaguchi [3]		Kustov et al. [8]	
Arata and Hino [4]		Adeeva et al. [9]	
Lavalley and co-workers [5]		Clearfield et al. [10]	
Riemer et al. [6]		Morterra et al. [11]	
White et al. [7]		Babou et al. [12]	

volves a tridentate bisulfate-like species. In contrast, Babou et al. [12] suggested sulfated zirconia to be sulfuric acid grafted at the zirconia surface. A compilation of these species is presented in Table 1 as an overview for a starting point of discussion.

IR spectroscopy [13] and calculations based on density-functional theory [14] demonstrated that several kinds of sulfur species could be present on sulfated zirconia. It is, however, also suggested that caution should be taken when linking such spectroscopic studies, since the information derived could originate from "spectator" sulfate groups [15].

The problem is complicated by the fact that sulfated zirconia is a very sensitive material and many variants may exist, despite the fact that industrial catalysts have been developed [16,17]. Thus, we have decided to revisit the problem of the nature of the catalytically active surface and the elementary steps of alkane activation on these materials in a larger team of several groups addressing the problem rigorously in a multitude of approaches ranging from surface science via model catalysts to explore industrial catalysts.

In this study, we present here for the first time direct evidence that in a commercial sample of active sulfated zirconia only a part of the sulfate groups, which can be removed by water washing, are the key elements for active species able to convert light alkanes at low temperatures. In order to preliminary characterize and understand the nature and function of the labile sulfate, activated samples and those in contact with adsorbed probe molecules were investigated with IR spectroscopy and a variety of physicochemical techniques and tested for the isomerization of *n*-butane.

2. Experimental

2.1. Catalyst preparation

Sulfate-doped zirconium hydroxide was obtained from Magnesium Electron, Inc. (XZO 1077/01). The received material was heated up to 873 K with an increment of 10 K/min in static air and kept at 873 K for 3 h. This material is denoted as SZ in the following.

To wash this calcined material 20 g of SZ was suspended in 400 ml bidistilled water for 20 min and then filtered. The washing procedure was repeated 3 times. Then, the filter cake was dried at room temperature. The resulting powder is denoted as SZ-WW.

2.2. *Catalyst characterization*

The BET surface area and pore size of sulfated zirconias were determined using a PMI automated BET sorptometer at 77.3 K using nitrogen as sorbate gas.

The sulfate content (SO_4^{2-} mmol/g) of the catalysts was determined using ion chromatography (IC) as described in Ref. [18]. For this, 0.02 g of sulfated zirconia was suspended in a 0.01 N solution of NaOH for 20 min. Then, the solution was filtered through a 0.45-µm filter. The sulfur content in the liquid was determined by the ion chromatography (Metrohm, 690 ion chromatograph equipped an IC anion column).

The XRD patterns of the sulfated zirconias were measured with a Philips X'Pert-1 XRD powder diffractometer using Cu-Kα radiation.

IR spectra of catalyst samples were collected using a Bruker IFS 88 (or alternatively a Perkin-Elmer 2000) spectrometer at 4 cm^{-1} resolution. Self-supporting wafers with a density of 5–10 mg/cm^2 were prepared by pressing the sample. The wafers were placed into in a stainless-steel cell with CaF_2 windows, heated up gradually with 10 K/min to 673 K in a flow of helium (10 ml/min), and held at that temperature for 2 h. A spectrum was recorded after the temperature was stabilized at 373 K. For adsorption of pyridine and CO_2 the experiments were conducted in a high vacuum cell with a base pressure of 10^{-6} mbar. The sample wafer was heated up gradually with a rate of 10 K/min to 673 K and held at that temperature for 2 h. The samples were exposed subsequently to 0.1 mbar pyridine at 373 K and to 2 mbar CO_2 at ambient temperature. Subsequent evacuation and thermal treatments are described under Section 3.

2.3. *n-Butane isomerization*

Isomerization of *n*-butane was carried out in a quartz microtube reactor (8 mm inner diameter) under atmospheric pressure. Sulfated zirconia pellets (0.2 g, 355–710 µm) were loaded into the reactor and activated in situ at 673 K for 2 h in He flow (10 ml/min). Then, the catalyst was cooled to 373 K and the reactant mixture (5% *n*-butane in He, total flow of 20 ml/min) was passed through the catalyst bed. The *n*-butane (99.5%, Messer) reactant was passed through an olefin trap containing activated HY zeolite (20 g) before it was mixed with He in order to remove olefin impurities and traces of water. Traces of butenes were not detected in the reactant mixture after purification. The reaction products were analyzed on-line using an HP 5890 gas chromatograph equipped with a capillary column (PLOT Al_2O_3, 50 m × 0.32 mm × 0.52 mm) connected to a flame ionization detector (FID).

3. Results and interpretation

3.1. *Chemical and physicochemical properties*

The sulfate content (SO_4^{2-} mmol/g), the (BET) specific surface area, and the average pore size are compiled in Table 2. The calcined sulfated zirconia (SZ) and the water-washed sample (SZ-WW) have high specific surface areas of 109 and 130 m^2/g, respectively. It is important to note that the surface-bound sulfate of calcined commercial sulfated zirconia is partially water soluble. This is clearly seen in the fact that the sulfate content of the water-washed sample (SZ-WW) was 0.25 mmol/g, while the parent sample (SZ) had 0.44 mmol/g. This difference indicates that approximately 40% of the total sulfate can be removed by washing with water as described.

The XRD pattern of SZ (see Fig. 1) is characteristic of pure tetragonal zirconia. Washing with water reduced the fraction of the tetragonal phase and induced the appearance of a monoclinic phase in SZ-WW.

3.2. *IR spectroscopy*

3.2.1. *Surface hydroxyl and sulfate groups of the activated samples*

The IR spectra of sulfated zirconia (SZ) and water-washed sulfated zirconia (SZ-WW) samples activated in He up to 673 K are shown in Fig. 2, which were normalized by the thickness of the wafers. The SZ sample

Table 2
Physical properties of sulfated zirconia samples

Sample	BET area (m^2/g)	Sulfate content SO_4^{2-} (mmol/g)	Pore size (nm)
SZ	109	0.44	3.6
SZ-WW	130	0.25	3.6

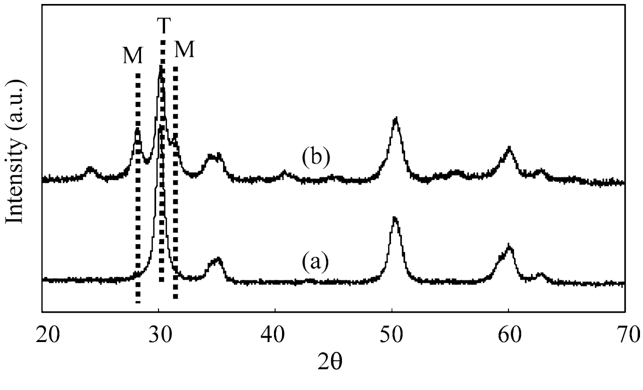


Fig. 1. XRD profiles of sulfated zirconias (a) SZ; (b) SZ-WW.

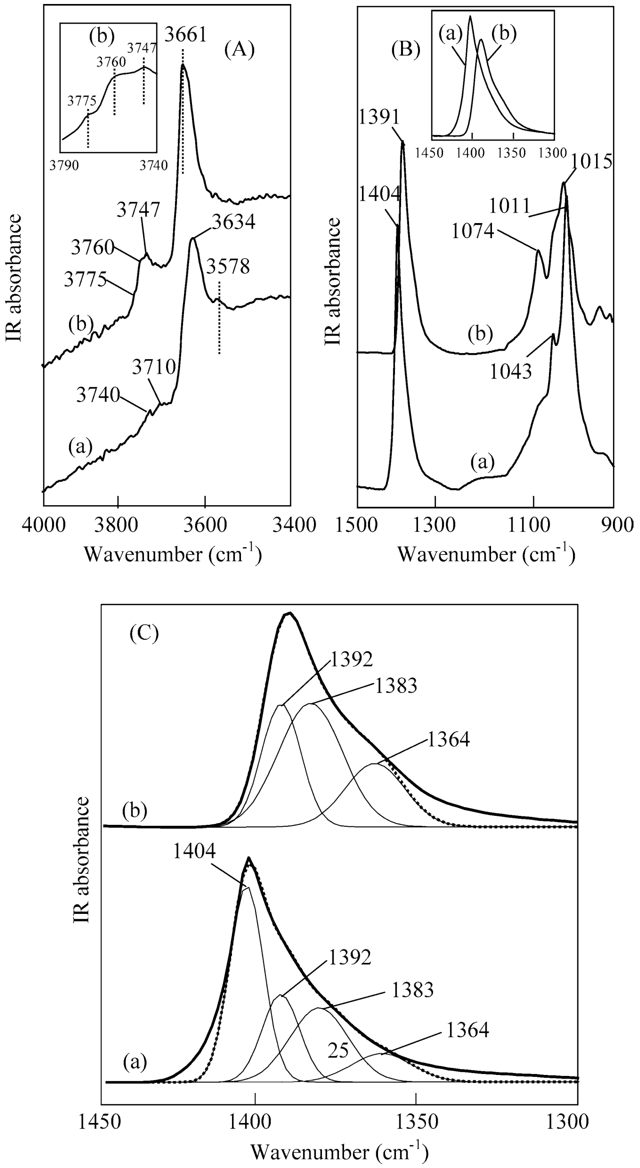


Fig. 2. IR spectra of sulfated zirconia samples at 373 K after in situ activation in He at 673 K for 2 h (a) SZ; (b) SZ-WW.

showed a weak band at 3578 cm^{-1}, a strong asymmetric band at 3634 cm^{-1} with a shoulder at 3660 cm^{-1}, and very weak bands at 3740 and 3710 cm^{-1}. Washing with water (SZ-WW, see Fig. 2A(b)) led to the disappearance of the bands at 3578 and 3634 cm^{-1} and to an increase in the intensity of the OH band at 3660 cm^{-1}. In addition, a group of small bands at 3747 and 3760 cm^{-1} with a shoulder at 3775 cm^{-1} was also observed (see the insert in Fig. 2A).

For activated zirconia, two bands attributed to the OH groups have been reported [19,20]. The higher frequency band ($\sim$ 3760 cm^{-1}) is attributed to terminal OH groups, which are single-coordinated to the ZrO_2 surface. The lower frequency band ($\sim$ 3680 cm^{-1}) is attributed to the bridging OH groups, which are bi- or tricoordinated to the zirconia surface. The broad band at 3500 to 3600 cm^{-1} is attributed to strongly hydrogen-bonded OH groups [19].

The increase in the bands of terminal and bridged OH groups after water washing indicates that the removal of water-soluble sulfate groups induces more sites for generating zirconia surface OH groups. The lower wavenumber of the bridged OH group in the presence of water-soluble sulfate (compared to the wavenumber of OH groups in the water washed sample) is attributed to the surface inductive effect of the sulfate group via electron withdrawal and bond polarization [21]. The multiplicity of components in the 3500–3800 cm^{-1} region is attributed to surface heterogeneity. In the presence of water-soluble sulfates, a weak, broad band at 3578 cm^{-1} characteristic of hydrogen-bonded OH groups was observed after activation. The minor bands at 3740 and 3710 cm^{-1} in IR spectrum of SZ are attributed to tetragonal terminal OH groups. New bands at 3760 and 3775 cm^{-1} were observed in IR spectrum of SZ-WW, characteristic of monoclinic terminal OH groups [19]. This is consistent with the XRD result that water washing leads to the phase transformation of tetragonal to monoclinic zirconia.

The IR spectra of sulfate groups of these two samples after activation are shown in Fig. 2B. Both spectra exhibit two groups of bands at 1300–1450 and 900–1150 cm^{-1}, which is in good agreement with the IR spectra of sulfated zirconia reported previously [22,23]. The group of bands between 1300 and 1450 cm^{-1} is attributed to S=O stretching vibrations of sulfate groups. The bands at 900–1150 cm^{-1} are assigned to the vibrations of S–O bonds of sulfate species connected to the zirconia surface.

The S=O stretching band of SZ was located at a rather high frequency, with a pronounced maximum at 1404 cm^{-1} and a broad portion to the low-frequency side. The spectrum of SZ-WW sample showed the maximum of this band at 1391 cm^{-1} and the intensity was lower than with SZ. The insert in Fig. 2B shows the S=O stretching bands of these two samples. The IR bands of S=O vibration of SZ and SZ-WW were fitted using a minimum number of bands with constant wavenumbers and half widths (see Fig. 2C).

The deconvolution results reveal that water washing reduces the portion of sulfate groups at the higher frequency (1410–1390 cm^{-1}) in the region of S=O stretching vibration of sulfate groups. Higher wavenumbers of the S=O stretching vibration indicate a higher S=O bond order [24,25]. Therefore, we conclude that water washing reduces the fraction of the most covalent sulfate. In addition to the changes of the S=O vibration band, the intensity of the S–O stretching vibration bands also decreased and shifted to higher wavenumbers after water washing (see Fig. 2B). SZ showed the S–O band at 1011 cm^{-1} with a minor contribution at 1043 cm^{-1}, while in the IR spectrum of activated SZ-WW the bands appeared at 1015 and 1074 cm^{-1}, respectively. Thus, the separation of the S=O and S–O vibrations is larger in the water-soluble fraction than in the sulfate groups after washing.

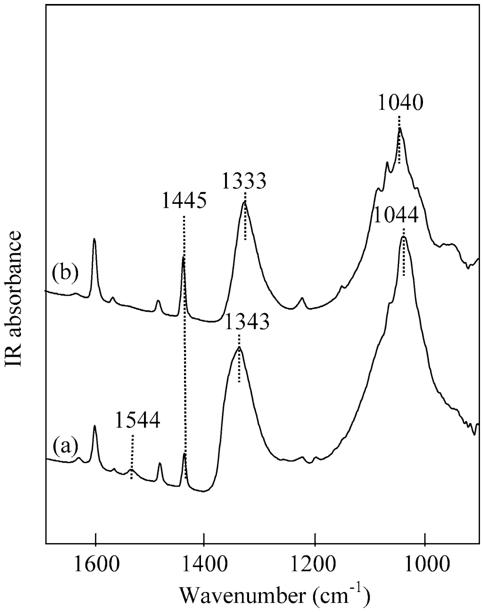


Fig. 3. IR spectra of pyridine (0.1 mbar) adsorption followed by evacuation at 373 K on sulfated zirconia samples activated in vacuum at 673 K for 2 h (a) SZ; (b) SZ-WW.

Table 3
Concentration of Brønsted and Lewis acid sites relative to pyridine adsorption/evacuation on sulfated zirconia samples

Sample	Brønsted acid (mmol/g)	Lewis acid (mmol/g)
SZ	0.050	0.106
SZ-WW	0	0.163

3.2.2. *IR spectra of adsorbed pyridine*

IR spectra of adsorbed pyridine on SZ and SZ-WW at 373 K followed by evacuation at the same temperature are shown in Fig. 3. Bands at 1445 and 1544 cm^{-1} indicate that after activation in vacuum at 673 K, Lewis and Brønsted acid sites are present on SZ. On SZ-WW only the band at 1445 cm^{-1}, characteristic for Lewis acid sites, was detected. The concentrations of the acid sites of these two samples are compiled in Table 3 using molar absorption coefficients of the bands of adsorbed pyridine equal to those determined for zeolites [26]. The concentrations of acid sites of these two samples demonstrate that water washing removes the Brønsted acid sites of sulfated zirconia and increases the Lewis acid sites from 0.106 to 0.163 mmol/g. It is interesting to note that for the two samples reported here, the total concentration of Lewis and Brønsted acid sits was nearly constant (0.16 mmol/g). This suggests that Brønsted and Lewis acid sites on the sulfated zirconia samples investigated are related.

As shown in Fig. 3, a marked shift of the band of S=O vibration after pyridine adsorption indicates a strong impact of the adsorbed pyridine molecule on the sulfate. A similar effect has been reported previously [27,28]. Note that the pyridine–sulfate interaction shifts all components of the S=O bands to lower wavenumbers, i.e., to 1343 cm^{-1} for SZ and to 1333 cm^{-1} for SZ-WW, which indicates that all sulfate groups are located at the metal oxide surface and are influenced by or interact with pyridine. The band of the S–O vibration shifted approximately 30 cm^{-1} to higher wavenumbers after pyridine adsorption. It indicates that the spectral separation between S=O and S–O decreased further by the interaction with the base. It can be speculated that the ionic character of the group increased in that process.

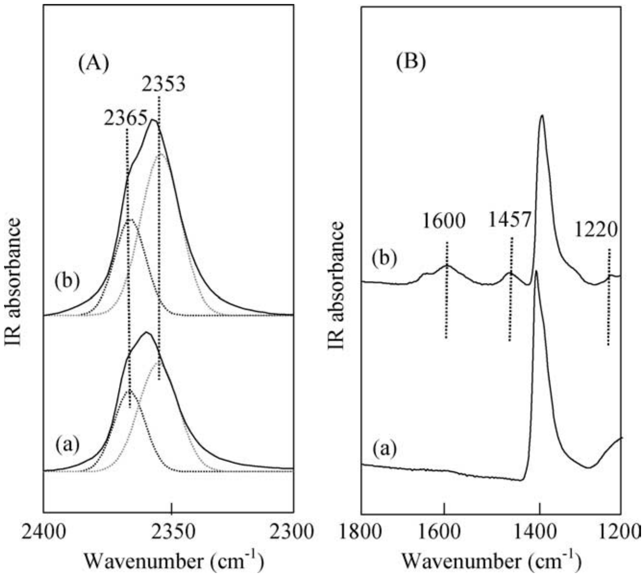


Fig. 4. IR spectra of 2 mbar CO_2 adsorption at room temperature on sulfated zirconia samples activated at 673 K in vacuum for 2 h (a) SZ; (b) SZ-WW.

3.2.3. *IR spectra of adsorbed CO_2*

CO_2 is a suitable probe for characterizing the surface basicity of a metal oxide system [29,30]. The carbonate species formed after adsorption give rise to bands between 2000 and 1000 cm^{-1}. However, CO_2 is also a weak base, which can reversibly form weakly (and linearly) coordinated species with Lewis acid sites. Thus, CO_2 adsorption at room temperature can be used to probe base sites and the strongest fraction of Lewis acid sites.

Fig. 4 shows the IR spectra of SZ and WW-SZ (activated in vacuum for 2 h at 673 K) after equilibration with 2 mbar CO_2 at room temperature. With both samples bands at 2353 and 2365 cm^{-1} attributed to linearly coordinated CO_2 were observed. As the upward shift of the asymmetric stretching band of adsorbed CO_2 is related to the strength of the bonding by the Lewis acid site [30], we conclude that the Lewis acid strength is not changed in the presence or absence of labile sulfate groups. The intensity of the band of adsorbed CO_2 on SZ-WW, however, is significantly higher than that on SZ, indicating a significantly higher concentration of Lewis acid sites on SZ-WW.

With SZ, bands between 1800 and 1200 cm^{-1} characteristic for carbonates were not observed. With SZ-WW, two pronounced bands at 1600 and 1457 cm^{-1} with another minor band at 1220 cm^{-1} characteristic of bicarbonate were

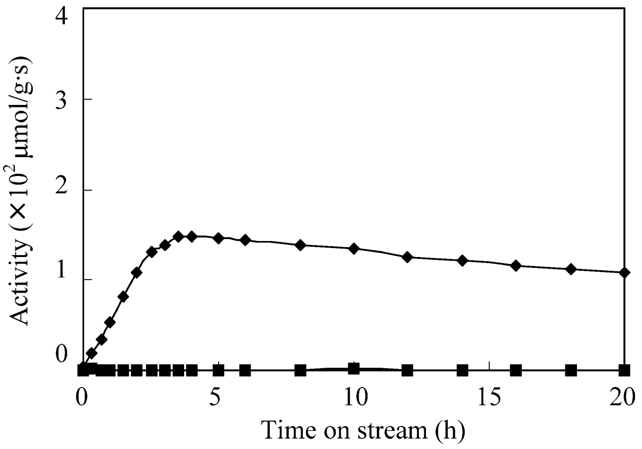


Fig. 5. *n*-Butane skeletal isomerization reaction (5% *n*-butane in He, 20 ml/min) rate versus time on stream on activated sulfated zirconias at 373 K (■) SZ-WW, (◆) SZ.

observed. This implies that removing the water-soluble sulfate by washing strongly increased the concentration of basic sites on the surface of the resulting material.

3.3. *Catalytic activity for n-butane skeletal isomerization*

Fig. 5 shows the catalytic activity versus time on stream for *n*-butane skeletal isomerization at 373 K on SZ and SZ-WW. It should be emphasized that great care has been taken to remove all traces of butenes from *n*-butane, as such impurities (causing much higher activity) lead to uncontrollable behavior and mask differences between the catalysts. The butenes impurity in *n*-butane in this study was below 1 ppm (undetectable by the GC analysis used).

Under the reaction conditions employed an induction period of approximately 4 h was observed. It has been suggested that carbenium ion-type intermediates, formed by protonation of butene, accumulate on the catalytic surface during this period [31]. After the induction period, SZ shows a maximum catalytic activity of 0.015 μmol/g s with an iso-butane selectivity of 96%. The variation of reaction conditions reported in the literature (reaction temperature, butane concentration, atmosphere, etc.) unfortunately makes directly comparing the reaction rates nearly impossible.

The problem of the direct comparison is well illustrated by the data of Song and co-workers [31] and Davis and co-workers [32] performing the reaction at 363 and 373 K. Davis and co-workers report the maximum activity to be approximately 40 μmol/g s, which is orders of magnitude higher than our results. The higher activity is attributed to the presence of 4000 ppm butene in *n*-butane. It is interesting to note in this context that these authors also demonstrated that removal of olefin impurities with 2 g of activated SZ induced an extremely low activity for a short period before the materials became totally inactive.

The removal of the water-soluble sulfate fraction on calcined sulfated zirconia resulted in a sample (SZ-WW) which was inactive for *n*-butane skeletal isomerization at 373 K.

4. Discussion

All sulfate species of sulfated zirconia are highly covalently bound to the surface compared to the inorganic sulfate salts, which can be clearly inferred from the differences in the IR spectra of ionic SO_4^{2-} (band between 1050 and 1250 cm^{-1}) and surface-bound sulfate (bands centered at 1200 cm^{-1}) [21]. Together with the partial hydroxylation, the higher covalence of the sulfate groups has been affiliated with the high acid strength of sulfated zirconia.

The S=O bands of sulfates were observed at 1404 cm^{-1} for SZ and at 1391 cm^{-1} for SZ-WW, suggesting that the labile sulfate species in SZ is more covalent than the water-insoluble sulfate of the SZ-WW sample. The IR spectra also showed that the highly covalent (labile) sulfate has a large spectral separation of the vibration of S=O and S–O bands, which indicate that the bonding electrons in the sulfate groups are relatively well localized, compared to the symmetric inorganic sulfate (one broad band between 1200 and 1100 cm^{-1}). The downward shift of the sulfate S=O band and the upward shift of the S–O band upon interaction with pyridine are attributed to an increase in the ionic properties of sulfate generated by the interaction with a base molecule.

The removal of the labile fraction of the sulfate induces the formation of bicarbonates, when the sample is exposed to CO_2. This indicates that the base strength of at least a fraction of the surface is as high as that of pure ZrO_2, as the carbonate formed on SZ-WW is identical with the carbonates on pure ZrO_2. From this we conclude that the removal of a fraction of the sulfate has led to parts of the surface being bare of sulfate groups.

A consensus has been reached that active sulfated zirconia, when evacuated at 300–450 °C possessed not only Lewis but also Brønsted acid sites. The nature and formation of the Brønsted acid sites on sulfated zirconia are, however, still debated. Ward and Ko [33] proposed that the strong Brønsted acidity of sulfated zirconia is generated from the surface OH group and that the proton-donating ability was enhanced by the electron-inductive effect of the S=O group. On the other hand, Kustov et al. [8] and Adeeva et al. [9] attributed the formation of Brønsted acid to the surface bisulfate species instead. Consensus has been reached, however, that the surface-coordinated unsaturated zirconium (CUS Zr^{4+}) of zirconia is responsible for the formation of the Lewis acid sites.

It is striking that the washing procedure led to an increase in the concentration of Lewis acid sites. Adsorbed pyridine and CO_2 indicate that the strength of the Lewis acid sites is similar for SZ and SZ-WW. With both probe molecules the wavenumbers of the characteristic bands of the adsorbed species were identical with both samples explored. This is important as it resolves an old conflict with respect to the role of Lewis acid sites for catalysis.

In previous reports [34,35], the catalytic activity of sulfated zirconia has also been attributed to the presence of Lewis acid sites, whose strength is enhanced by the electron-withdrawing sulfate groups. Here, we demonstrate two samples with exactly the same Lewis acid strength, SZ and SZ-WW. However, SZ-WW is inactive despite a higher concentration of Lewis acids sites of equal strength. Therefore, we conclude that Lewis acid sites are not directly involved in the isomerization of alkanes by sulfated zirconia at low temperature.

The increase in the concentration of Lewis acid sites by water washing, on the other hand, indicates that at least some of the labile sulfate groups are located on top of Lewis acid sites, presumably at the defect sites of the zirconia surface. By interaction with the sulfate groups, those sites are saturated and Lewis acidity is lost. Thus, the presence of the labile sulfate groups on the surface diminishes not only the basic sites, but also a portion of Lewis acid sites. The fact that the sum of Brønsted and Lewis acid sites remains constant for the two samples suggests that the Brønsted acid sites are affiliated with sulfate groups covering Lewis acid sites. It also demonstrates unequivocally that Brønsted acid sites are indispensable for the skeletal isomerization of n-butane.

5. Conclusions

At least two types of sulfate groups exist on the surface of active sulfated zirconia. One of those types of sulfate groups can be removed by washing with water at ambient temperatures. Approximately 40% of the sulfur in the sulfated zirconia can be removed in this way. A fraction of the sulfate removed via this way is located on top of a Lewis acid site (coordinatively unsaturated Zr^{4+}), which has a more covalent S=O bond than all species remaining on the surface after washing. It can be clearly identified by a narrow S=O band at 1404 cm^{-1}. The hydroxyl groups affiliated with these labile sites and the sites of the catalytically active Brønsted acid sites are characterized by a broad IR band characteristic of hydrogen-bonded OH groups. The exact nature of this site is not a subject of the present contribution. It is shown, however, that the OH groups of ZrO_2 are not involved in the catalysis and in the generation of strong Brønsted acid sites able to protonate pyridine.

The catalytic isomerization of n-butane requires the labile sulfate. In the absence of the labile sulfate the material is completely inactive for n-butane isomerization at 373 K. Because the washing procedure increases the concentration of Lewis acid sites without decreasing their strength, we can unequivocally conclude that Lewis acid sites of sulfated zirconia are insufficient to catalyze n-butane isomerization. We conclude in consequence that Brønsted acid sites affiliated with the labile sulfate groups are indispensable for this reaction.

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