Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Catalysis 238 (2006) 39–45

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Synthesis of highly active sulfated zirconia by sulfation with SO_3

Xuebing Li [1], Katsutoshi Nagaoka [2], Roberta Olindo, Johannes A. Lercher *

Technische Universität München, Lehrstuhl für Technische Chemie II Lichtenbergstraße 4, 85747 Garching, Germany

Received 26 October 2005; revised 25 November 2005; accepted 28 November 2005

Available online 22 December 2005

Abstract

Highly active sulfated zirconia (SZ) materials were prepared by sulfation of crystalline zirconia with gaseous SO_3. This direct method circumvents the use of liquid sulfation agents, as well as a final calcination step. The amount of sulfur species retained by SO_3-SZ samples was directly proportional to the fraction of monoclinic phase and the concentration of Brønsted acid sites. However, the catalytic activity in n-butane isomerization at 373 K was proportional to the concentration of labile chemisorbed SO_3, most likely in the form of pyrosulfate species showing a characteristic IR band at 1404 cm^{-1}. Tetragonal zirconia favors the formation of these labile sulfur species, playing a key role in light alkane activation.

Keywords: Sulfated zirconia; Butane isomerization; SO_3 sulfation; Activity; Labile sulfate

1. Introduction

Sulfated zirconia (SZ) and other sulfated metal oxides have been studied for more than two decades because of their high catalytic activity for activation of short alkanes at low temperatures. The catalytic properties of sulfated metal oxides depend strongly on subtle variations in the material. The influence of preparation parameters on catalytic activity has been thoroughly discussed in the literature, particularly the zirconia precursor [1], the sulfation procedure [2], and the calcination treatment [3,4]. Three conditions are generally recognized as indispensable for the preparation of an active catalyst: (i) the treatment with liquid sulfating agents must be performed on amorphous zirconium hydroxide, the sulfation of crystalline zirconia being ineffective [5]; (ii) only the tetragonal or cubic ZrO_2 phases are active, whereas the monoclinic is nearly inactive [6,7]; and (iii) a final calcination at high temperatures is a crucial step in the formation of active sites [8–10].

In contrast, a recent study found aqueous sulfation of crystalline zirconia stabilized in the tetragonal or cubic forms by formation of a solid solution with Y_2O_3 to be an effective method for preparation of catalytically active SZ [11]. In agreement with the literature, sulfated monoclinic zirconia was reported to be hardly active for butane isomerization.

One-step synthesis of moderately active monoclinic SZ catalyst was reported by Stichert et al. [12]. However, the corresponding sample exhibited a lower catalytic activity than tetragonal materials, and the authors concluded that even if the crystal phase plays a role with respect to the activity of SZ, it is not as crucial as generally thought. Synthesis of active monoclinic SZ catalysts has also been reported by others [13,14]; however, the catalysts had nonnegligible amounts of tetragonal zirconia and in every case the catalytic activity of the monoclinic samples was much lower than that of tetragonal SZ.

Whatever the ZrO_2 phase used, a final calcination step has been recognized as being critical for the formation of active sites. Some claim that high-temperature treatment forms active sites by effectively binding sulfate groups to the zirconia surface [8,9]. Others proposed that another important function of the calcination step is the partial removal of sulfate species from highly uncoordinated sites on ZrO_2, creating strong Lewis acid

---

* Corresponding author. Fax: +49 0 89 289 13544.
E-mail addresses: roberta.olindo@ch.tum.de (R. Olindo), johannes.lercher@ch.tum.de (J.A. Lercher).

[1] Present address: Department of Chemical Engineering, University of California at Berkeley, Berkeley, CA 94720, USA.

[2] Present address: Department of Applied Chemistry, Faculty of Engineering, Oita University Dannoharu 700, Oita 870-1192, Japan.

0021-9517/$ – see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2005.11.039

sites. The strength of these (potentially catalytically active) acid sites is said to be enhanced by the electron-withdrawing effect of the neighboring sulfate groups [10,11].

Preparation of SZ by sulfation of crystalline metal oxides with gaseous SO_3 has been reported. Yamaguchi et al. [15] demonstrated that strong acid sites are generated on Fe_2O_3 by sulfation with SO_3 at 573 K, with the final catalyst being active for cyclopropane isomerization. Recently, Haw et al. [16,17] noted the formation of Brønsted acid sites on zirconia by SO_3 chemisorption using NMR spectroscopy and theoretical studies.

The present study explores new materials based on sulfated crystalline zirconia with gaseous SO_3. The procedure that we have developed is the first to allow us to independently vary solid-state properties, such as phase composition and sulfate loading, which can provide insight into more conventional sulfate-based catalysts. In addition, materials prepared by in situ sulfation with SO_3 were compared with materials prepared by ex situ sulfation, to investigate the influence of very labile sulfate groups on the catalytic activity for *n*-butane isomerization.

2. Experimental

2.1. Catalyst preparation

Sulfate-doped zirconium hydroxide was obtained from Magnesium Electron (XZO 1077/01). The received material was calcined up to 873 K at a rate of 10 $K\,min^{-1}$ in static air and kept at this temperature for 3 h. The final sample is denoted as SZ henceforth.

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

The sulfate species were extracted from 20 g of SZ using 400 ml of NaOH 0.05 M. After filtration, the cake was washed carefully for several times with bi-distilled water to remove the residual NaOH. The resulting material is pure zirconia, denoted as SZ-BW.

Plain zirconia (ZrO_2) used in this study was prepared by calcination of commercial zirconium hydroxide ($Zr(OH)_4$, Aldrich) in flowing air at 873 K for 3 h at an increment of 10 $K\,min^{-1}$.

Sulfation by gaseous SO_3 was performed in a quartz tube ("ex situ sulfation" with respect to the catalytic tests). Before gaseous SO_3 was admitted, SZ or zirconia (pellets, 355–710 µm, 0.5–2 g) were preheated in the quartz tube under N_2 flow (50 $ml\,min^{-1}$) at 673 K for 2 h, then cooled to 473 K. The SO_3 cylinder was then filled with 50 ml of N_2 via valve 1 (Fig. 1) and subsequently connected to the flow system. SO_3-saturated nitrogen (50 ml) was flown through the quartz tube together with the carrier gas (N_2, 50 $ml\,min^{-1}$) for 1 h. Samples of all materials were sulfated following the above-described procedure and finally stored in a desiccator. We call these samples SZ-SO_3, SZ-WW-SO_3, SZ-BW-SO_3, and ZrO_2–SO_3.

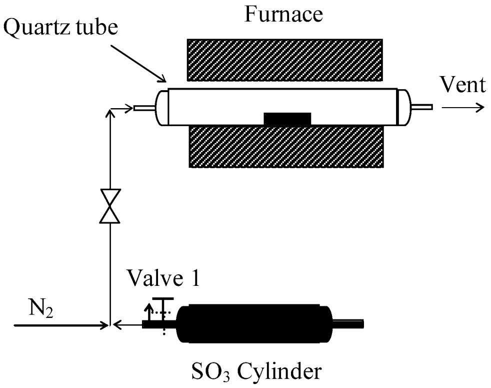

Fig. 1. Scheme of sulfation ex situ with gaseous SO_3 on crystalline zirconia materials.

Sulfation of SZ with SO_3 was also performed in the reactor ("in situ sulfation"), to investigate the influence of rehydration and activation between sulfation and catalytic tests. The in situ sulfated SZ sample is denoted as SZ-SO_3 in situ. First, 0.2 g of SZ was heated for 2 h at 673 K (at a rate of 10 $K\,min^{-1}$) in He (10 $ml\,min^{-1}$) and then cooled to 373 K. Subsequently, 50 ml of He saturated with SO_3 at room temperature were flushed over the catalyst at 373 K. After purging with He (10 $ml\,min^{-1}$) for 0.5 h, *n*-butane isomerization was studied at this temperature.

2.2. Catalyst characterization

The sulfate content of the catalysts was determined by ion chromatography (IC) as described previously [18]. Typically, 0.02 g of SZ was suspended in 20 ml of 0.01 M NaOH for 20 min. The solution was filtered through a 0.45-µm filter, and the sulfur content in the liquid was determined by IC using a Metrohm 690 ion chromatograph. The BET surface area and the pore volume of the samples were determined by physisorption of N_2 at 77 K using a PMI automated BET-sorptometer.

X-Ray diffraction (XRD) patterns were collected with a Philips X'Pert-1 XRD powder diffractometer using Cu-K_α radiation. The fraction of tetragonal zirconia (X_t) was calculated using the following equation:

$$X_t = I_t(111)/(I_m(111) + I_t(111) + I_m(11\bar{1})).$$

IR spectra of the 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. The wafers were placed into in a stainless steel cell with CaF_2 windows, gradually heated at a rate of 10 $K\,min^{-1}$ to 673 K in He flow (10 $ml\,min^{-1}$), and held at that temperature for 2 h. A spectrum was recorded after the temperature was stabilized at 373 K. For adsorption of pyridine, the experiments were conducted in an evacuable cell. The sample wafer was heated at a rate of 10 $K\,min^{-1}$ to 673 K and held at that temperature (base pressure of 10^{-6} mbar) for 2 h. The sample was exposed to 0.1 mbar of pyridine at 373 K and outgassed at the same temperature.

2.3. Butane isomerization

n-Butane isomerization was carried out in a quartz microtube reactor (8 mm i.d.) under atmospheric pressure. 0.2 g of SZ pellet (355–710 µm) was loaded into the reactor and activated in situ at 673 K for 2 h in He flow (10 ml min^{-1}). The catalyst was cooled to 373 K, and the reactant mixture (5% *n*-butane in He; total flow, 20 ml min^{-1}) was fed through the catalyst bed. Butane (99.5%, Messer) was passed through an olefin trap containing activated H-Y zeolite (20 g) before being mixed with He. After purification, even traces of butenes were not detected in the reactant mixture (detection limit, 1 ppm). The reaction products were analyzed using an on-line HP 5890 gas chromatograph equipped with a capillary column (plot Al_2O_3, 50 m × 0.32 mm × 0.52 µm) connected to a flame ionization detector.

3. Results

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

Fig. 2 shows the catalytic activity versus time on stream for *n*-butane skeletal isomerization at 373 K on the parent sample (SZ), the water-washed sample (SZ-WW), and the ex situ SO_3 sulfated samples (SZ-SO_3 and SZ-WW-SO_3). SZ showed moderate catalytic activity with a selectivity of 96% to isobutane. Washing SZ with water (SZ-WW) removed the labile sulfate fraction and resulted in a completely inactive sample [19]. Sulfation of SZ with gaseous SO_3 (SZ-SO_3) drastically increased the catalytic activity, with the maximum activity of SZ-SO_3 being around 10 times that of SZ. After sulfation of the inactive SZ-WW sample with gaseous SO_3, the catalytic activity was lower, but close to that of SZ-SO_3.

The ex situ SO_3 sulfation technique was also applied to the two zirconia samples containing high concentrations of the monoclinic phase, ZrO_2 (70% monoclinic) and SZ-BW (94% monoclinic). The catalytic activity for *n*-butane isomerization of the two corresponding samples (ZrO_2–SO_3 and SZ-BW-SO_3) at 373 K is shown in Fig. 3. Contrary to the previous conclusion that the sulfation of crystalline monoclinic zirconia is not capable of generating active sites for *n*-butane isomerization [5], ZrO_2–SO_3 and SZ-BW-SO_3 exhibited slightly higher catalytic activity than that of SZ obtained by calcination of an amorphous sulfated zirconium hydroxide.

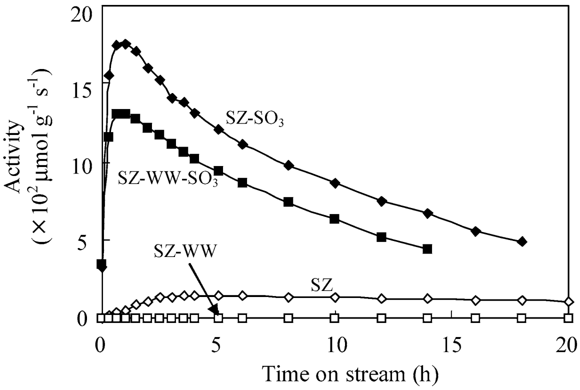

Fig. 2. *n*-Butane reaction rate versus time on stream on sulfated zirconia samples at 373 K (□) SZ-WW, (◇) SZ, (■) SZ-WW-SO_3 and (◆) SZ-SO_3. SO_3 gaseous sulfation was performed ex situ.

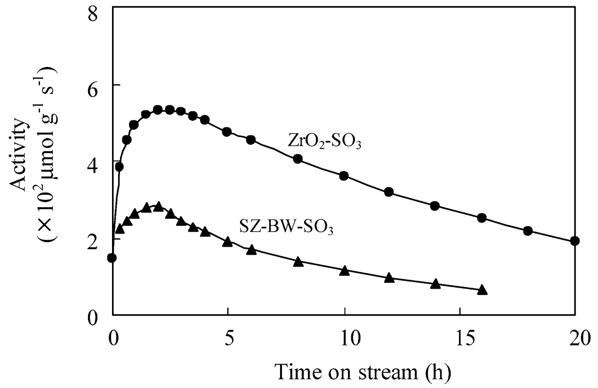

Fig. 3. *n*-Butane reaction rate versus time on stream on sulfated zirconia at 373 K (▲) SZ-BW-SO_3 and (●) ZrO_2–SO_3.

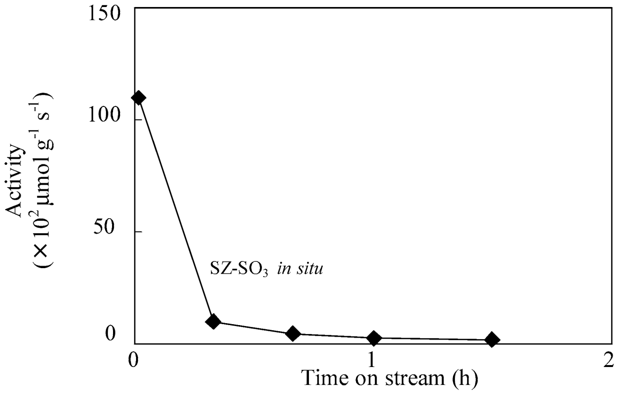

Fig. 4. *n*-Butane reaction rate versus time on stream at 373 K on in situ SO_3 sulfated SZ.

Although the ex situ SO_3 sulfated samples showed significantly enhanced catalytic activity compared with the parent material, we speculated that some of the very labile sulfate species could be lost during the activation treatment before testing the catalytic activity. To investigate this aspect, samples of the parent SZ were modified ex situ and in situ with SO_3, and the catalytic activities for *n*-butane isomerization were compared. As shown in Fig. 4, the SZ-SO_3 in situ sample showed very high initial catalytic activity, approximately two orders of magnitude higher than the maximum activity of SZ. However, all catalysts exposed in situ to SO_3 deactivated rapidly, related to oligomerization of olefins formed at higher concentration in the more active samples.

3.2. Physical properties

The BET area and sulfate content of the different zirconia samples are reported in Table 1. Both calcined commercial SZ and ZrO_2 had specific surface areas >100 $m^2\,g^{-1}$. Washing SZ with water removed approximately 40% of the initial sulfur species [19], whereas washing with dilute NaOH completely removed the sulfur species. As expected, sulfation with gaseous

Table 1
Physical properties of zirconia and sulfated zirconia samples

Sample	BET area ($m^2\,g^{-1}$)	Sulfate content SO_4^{2-} ($mmol\,g^{-1}$)	Tetragonal phase (%)	Acid sites ($mmol\,g^{-1}$)	
				Brønsted	Lewis
SZ	109	0.44	100	0.050	0.106
SZ-SO_3	n.d.	0.64	100	0.071	0.073
SZ-WW	n.d.	0.25	58	0	0.163
SZ-WW-SO_3	n.d.	0.91	58	0.113	0.054
SZ-BW-SO_3	n.d.	1.53	6	0.135	0.037
ZrO_2	123	n.d.	30	0	0.206
ZrO_2–SO_3	n.d.	1.15	30	0.173	0.089

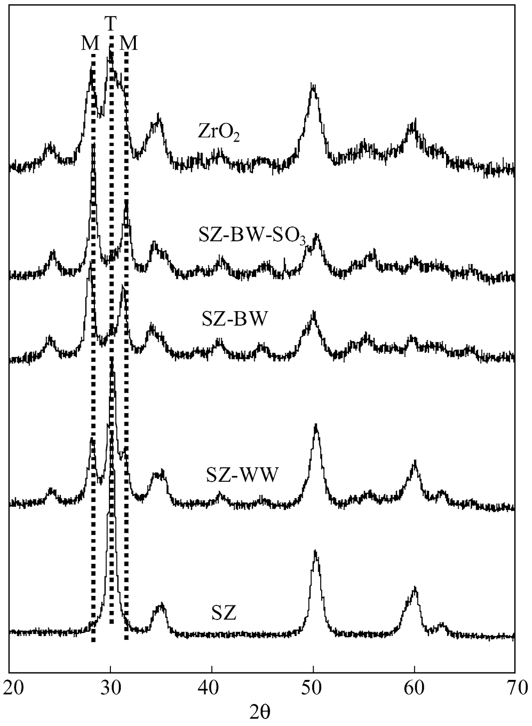

Fig. 5. XRD profiles of sulfated zirconias and zirconias. T: tetragonal, M: monoclinic.

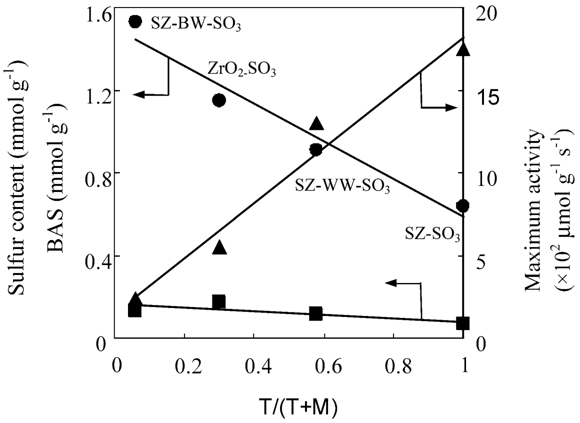

Fig. 6. Correlation among fraction of tetragonal phase $T/(T + M)$, (●) sulfur content, (■) Brønsted acid site concentration BAS and (▲) maximum catalytic activity for the SO_3 sulfated samples: SZ-SO_3, SZ-WW-SO_3, ZrO_2–SO_3 and SZ-BW-SO_3.

SO_3 increased the sulfate concentration on the parent material from 0.44 to 0.64 $mmol\,g^{-1}$ (SZ-SO_3). According to the surface area that a sulfate group occupies based on its kinetic diameter (0.31 nm^2) [20], the sulfate concentrations of all SO_3 sulfated samples exceed the monolayer coverage (0.58 $mmol\,g^{-1}$ for SZ-SO_3 and 0.66 $mmol\,g^{-1}$ for ZrO_2–SO_3).

As shown in Fig. 5, the zirconia in the SZ sample was mainly tetragonal. Water washing reduced the fraction of the tetragonal phase and induced transformation to the monoclinic phase (42%) [19]. Moreover, after removal of all sulfate groups by washing with NaOH, the resulting material, SZ-BW, was nearly exclusively monoclinic (94%). Sulfation with SO_3 did not influence the XRD pattern of the parent sample SZ-BW.

Fig. 6 shows that the sulfate content of samples after SO_3 sulfation was directly proportional to the fraction of monoclinic phase present. The higher the fraction of monoclinic phase, the higher the concentration of sulfate groups. The concentration of sulfate groups on almost pure monoclinic zirconia (SZ-BW-SO_3) was nearly twice that of tetragonal zirconia (SZ-SO_3). This indicates that the monoclinic phase is able to retain more SO_3 than the tetragonal phase, suggesting that the monoclinic form may be more basic than the tetragonal.

3.3. *Characterization of acid base properties by in situ IR spectroscopy*

3.3.1. *IR spectra of surface hydroxyl groups*

Fig. 7A compiles the IR spectra, normalized by the wafer thickness, in the region of the surface OH stretching bands. Before the spectra were recorded, the samples were activated in He at 673 K for 2 h. The IR spectrum of SZ showed a moderately strong, asymmetric band at 3634 cm^{-1} with a shoulder at 3660 cm^{-1} and very weak bands at 3740 and 3710 cm^{-1}. In addition, a weak band located at 3578 cm^{-1} was also observed. Both samples that did not contain labile sulfate surface groups (SZ-WW and ZrO_2) showed a very strong IR band at 3600–3700 cm^{-1}, assigned to bridging OH groups [21,22], as well as OH bands between 3700 and 3800 cm^{-1} assigned to terminal OH groups [21,22]. SO_3 sulfation reduced the intensity of the OH bands above 3600 cm^{-1}, as shown in the spectra of SZ-SO_3, SZ-WW-SO_3, SZ-BW-SO_3, and ZrO_2–SO_3. The decrease in OH group concentration after SO_3 sulfation is tentatively attributed to the substitution of the surface OH groups of zirconia by SO_3. Thus SZ-BW-SO_3, which has the highest sulfate content among the SO_3-sulfated samples, did not exhibit OH bands above 3600 cm^{-1}. The samples containing labile sulfate species showed a band at 3570 cm^{-1}.

3.3.2. *IR spectra of surface sulfate groups*

The IR spectra of sulfate groups of the samples activated at 473 K are compiled in Fig. 7B. All of the samples showed stretching vibrations of the S=O group between 1300 and 1450 cm^{-1}. In accordance with previous assignations, the bands are attributed to highly covalent sulfate groups [23, 24]. The IR spectrum of SZ had the maximum of this band at 1404 cm^{-1}. After sulfation with SO_3 (trace SZ-SO_3), the

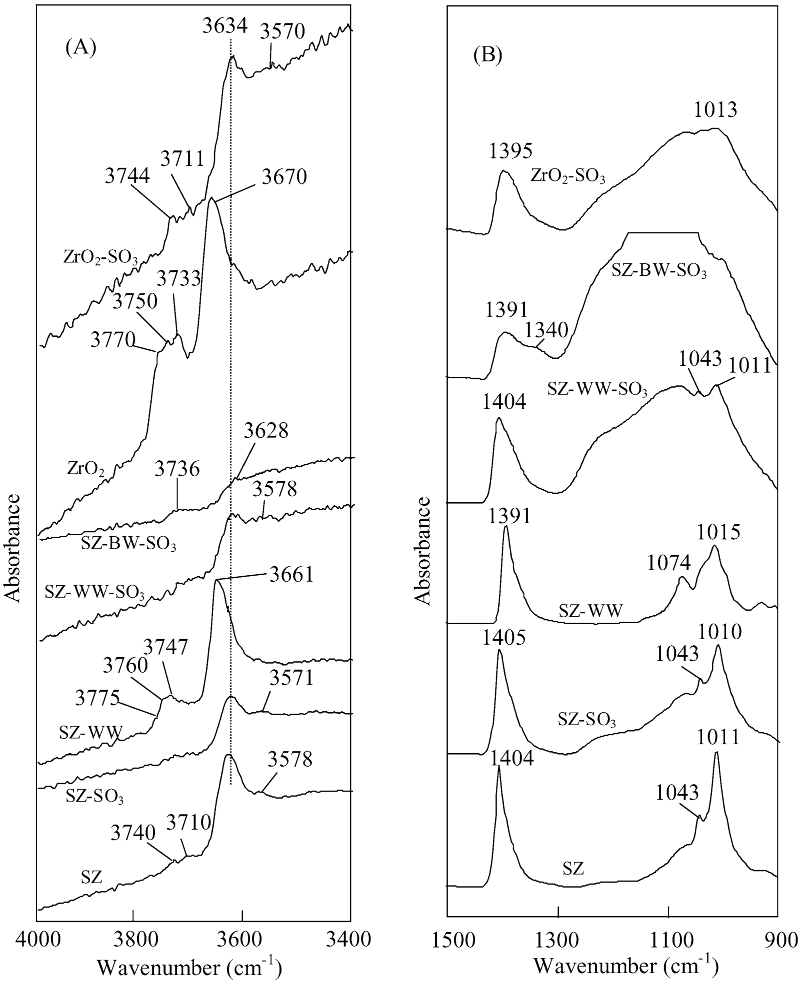

Fig. 7. IR spectra in the regions of surface OH group (A) and surface sulfate group (B) of sulfated zirconias and zirconia.

corresponding band was broader, but otherwise unchanged. A broad band appeared simultaneously in the 1300–1200 cm^{-1} region.

After washing with water (SZ-WW), the part of this complex band at higher wavenumbers (i.e., that at 1404 cm^{-1}) disappeared; as a result, the maximum of the band was shifted downward to 1391 cm^{-1} [19]. However, sulfation of the washed sample (SZ-WW-SO$_3$) restored the labile sulfate groups, as indicated by the reappearance of the peak at 1404 cm^{-1}. In the region of S–O vibration, two bands located at 1011 and 1043 cm^{-1} were observed in the spectra of SZ, SZ-SO$_3$, and SZ-WW-SO$_3$. The strong bands in the 1100–1300 cm^{-1} range in the IR spectra of SO$_3$-sulfated samples were ascribed to the surface polysulfate groups, which are related to the high sulfate content.

3.3.3. *Determination of acid sites by IR spectroscopy of adsorbed pyridine*

Pyridine is widely used as qualitative and quantitative probe to identify the concentration and nature of acid sites using the characteristic bands of pyridinium ions at 1540 cm^{-1}, as well as the band between 1440 and 1455 cm^{-1} characteristic for pyridine bound coordinatively to Lewis acid sites [25]. The concentrations of Brønsted and Lewis acid sites derived in this way are compiled in Table 1. For quantification, the molar absorption coefficients of the bands of adsorbed pyridine were set equal to those determined for zeolites [25].

The results compiled in Table 1 show that the water washing treatment removed all Brønsted acid sites together with water-soluble sulfate groups from SZ. Simultaneously, the concentration of Lewis acid sites increased [19]. This suggests that the labile sulfate groups are responsible for generating Brønsted acid sites and that they are at least partially bound to Lewis acid sites. In contrast, sulfation with SO$_3$ led to the restitution of the Brønsted acid sites (compare SZ-WW-SO$_3$ and SZ-SO$_3$ to SZ-WW and SZ) and the decrease in the concentration of Lewis acid sites. Thus, at least some of the chemisorbed SO$_3$ molecules lead to the labile sulfate groups coordinatively bound to Lewis acid sites. Note that SO$_3$ sulfation also induced Brønsted acidity on pure ZrO$_2$, which otherwise have only Lewis acid sites. With the exception of SZ-WW (having no Brønsted acid sites), the concentration of Brønsted acid sites of SZ is directly related to the sulfate concentration (see Fig. 6). We speculate, therefore, that the sulfate groups remaining after the washing procedure on SZ-WW either are not located at the outer surface or are bound in a from not permitting hydroxylation.

4. Discussion

Calcined SZ was active for *n*-butane skeletal isomerization at 373 K. Removal of the water-soluble sulfate by washing with water rendered the catalyst inactive even though approximately 60% of the sulfate species were retained [19]. In contrast, sulfation of the parent SZ with SO_3 induced very high catalytic activity, indicating that SO_3 deposition on the properly activated SZ generates more active sites. Sulfation with SO_3 on the inactive water-washed sample (SZ-WW) induced high activity.

Thus, the pronounced promoting effect of sulfation with SO_3 on the catalytic activity of SZ gives strong evidence that the labile sulfate species, generated by the adsorption of SO_3, are essential for the formation of active sites. This indicates that SO_3 must be adsorbed on or close to an existing, albeit inactive, sulfate group. Theoretical calculations suggest that the active sulfate species formed is a pyrosulfate group. These functional groups have been shown to initiate the catalytic cycle by providing olefins via oxidative dehydrogenation of *n*-butane [26,27]. A kinetic analysis suggests that the initial rate of isomerization is directly proportional to the rate at which these oxidizing sulfate sites generate butene [26].

The paramount role of the labile active sulfate species is also demonstrated by the difference between the catalysts sulfated in situ and those sulfated ex situ. The extremely higher initial activity of SZ after in situ sulfation compared with the catalytic material sulfated ex situ indicates that the concentration of the active sulfate species induced by chemisorbed SO_3 is dramatically increased. We attribute the difference to the significantly higher concentration of the oxidizing pyrosulfate groups in the case of the in situ sulfation. It should be noted that these labile sulfates are very sensitive toward thermal treatment, especially after rehydration under ambient conditions.

The importance of adsorbed SO_3 becomes clearer when comparing the activities of SZ calcined in a shallow bed with that calcined in a deep bed [28]. These calcination procedures were conducted under exactly identical conditions, with heating up to 873 K at a rate of 10 $K\,min^{-1}$ in static air and maintaining this temperature for 3 h. The only difference was the depth of the catalyst bed; in the shallow-bed configuration, the catalyst was spread out evenly on a ceramic plate, whereas in the deep-bed mode the catalyst had a bed depth of approximately 1 cm. SO_3 evolves during calcination; it largely escapes during shallow-bed calcination, but is at least partially captured by the upper layers in the bed. Note that, interestingly, the latter catalyst was an order of magnitude more active than the former. This demonstrates not only how important SO_3 is in forming an active catalytic material, but also how subtle variations of the catalyst preparation conditions may dramatically influence the activity, and hence the stability, of SZ.

Having demonstrated that the generation of the labile oxidizing sulfate groups by chemisorbing SO_3 is critical for generating an active catalyst, we now turn our attention to the role of the underlying substrate (i.e., the crystalline form of zirconia) in the formation of active pyrosulfate species. Sulfation with SO_3 of an almost monoclinic zirconia sample (SZ-BW) led to a sample (SZ-BW-SO_3) with catalytic activity close to that of the parent SZ. Nevertheless, it should be kept in mind that this activity is an order of magnitude lower that of SZ-SO_3, which was obtained by sulfation of the tetragonal sample SZ. Thus, it appears that the catalytic activity is primarily a function of the concentration of the labile sulfate groups, which in turn increases with increasing concentration of tetragonal zirconia.

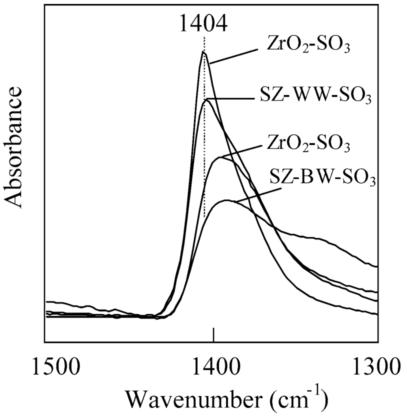

Fig. 8. IR spectra in the region of S=O stretching vibration of sulfated zirconias: SZ-SO_3, SZ-WW-SO_3, ZrO_2–SO_3 and SZ-BW-SO_3.

This supposition is supported by the data in Fig. 8 indicating that the intensity of the band characteristic of the labile sulfate/pyrosulfate group (1404 cm^{-1}) varies in parallel with the catalytic activity. The sample with the most intense band was the most active; that is, the activity for *n*-butane isomerization at 373 K was 0.175 $\mu mol\,g^{-1}\,s^{-1}$ on SZ-SO_3. SZ-BW-SO_3, having the lowest 1404 cm^{-1} band, was the least active sample (0.028 $\mu mol\,g^{-1}\,s^{-1}$).

The finding that catalytic activity depends strongly on the concentration of labile sulfate suggests that sulfate groups on monoclinic SZ should be more stable than sulfate groups on tetragonal SZ. This trend is also seen in the uptake of SO_3 on the various samples. Having exposed all samples to the exact same number of SO_3 molecules at the same temperature and SO_3 partial pressure, the uptake of SO_3 increased with increasing concentration of the monoclinic phase (Fig. 6). This suggests that stronger basic sites allow binding SO_3 more effectively on monoclinic zirconia than on tetragonal zirconia, but these more basic sites in monoclinic zirconia also reduce the formation of labile groups. In line with this reasoning, the catalytic activity and the fraction of tetragonal zirconia of the SO_3 sulfated samples are directly proportional.

The role of coexisting Brønsted and Lewis acid sites has been discussed extensively in the SZ literature [29–31]. The present results clearly show that the role of Lewis acid sites may be only to influence sulfate group formation, and it might not be actively involved in the catalytic process. In fact, pure zirconia (ZrO_2) and water-washed SZ (SZ-WW), which have only Lewis acid sites, are completely inactive. The adsorption of SO_3 leads to the decrease in the concentration of Lewis acid sites and the increase/formation of Brønsted acid sites. This suggests that a fraction of labile sulfate species is coordinately bound to Lewis acid sites. For a given group of supports, the concentration of Brønsted acid sites increases in parallel to the concentration of sulfate species (see Fig. 6). At the same time, the intensity of the bands corresponding to the terminal and bridging hydroxyl groups of ZrO_2 decrease dramatically after SO_3 sulfation. Although we do not wish to speculate on the nature of the newly formed OH groups, we would like to point to quantum chemical calculations [32] and suggest that the hydroxy groups in these models are related to hydroxylated pyrosulfate or bisulfate species [33,34].

In our study, sulfation with gaseous SO_3 has been successfully applied to already crystallized samples despite the presence/absence of sulfate groups before calcination and the crystallographic form of zirconia. SO_3 sulfation has been purposely applied to already crystallized samples to gain insight into the nature of the real sulfating agent (SO_3) and the function of the calcination procedure. It has been claimed that calcination of SZ precursors at high temperature by aqueous sulfation of an amorphous zirconium hydroxide or crystalline zirconia is a necessary step in generating active sites. This calcination is claimed to convert the amorphous zirconium hydroxide to tetragonal zirconia, to bind the sulfate groups with the zirconia surface [8,9,35], and in part to eliminate the excess sulfate groups from Lewis acid sites, that is, coordinately unsaturated Zr^{4+} [10,11]. The present study shows that sulfation with SO_3 at 473 K can generate active sites without calcination and that Lewis acid sites are primarily needed for binding SO_3. Thus, in the conventional preparation method using a liquid sulfating agent, the calcination of the sulfated precursor at high temperatures serves only to generate the SO_3 in situ so that it can be captured, forming pyrosulfate groups.

5. Conclusion

Sulfation with gaseous SO_3 has been shown to be an effective new approach for preparing highly active SZ. This novel method avoids complex preparation procedures and allows us to tailor the activity of the catalyst. Labile sulfate species are essential for the formation of active sites, which can be removed by water-washing treatment and recovered by SO_3 sulfation of crystalline zirconia materials. The decrease in Lewis acidity after SO_3 sulfation indicates that at least some of the labile sulfates are coordinately bound to the Lewis acid sites. The labile sulfate groups induce Brønsted acidity on the zirconia surface. The increase in Brønsted acid sites and the significant decrease in zirconia surface OH groups by SO_3 sulfation indicate that Brønsted acid sites are affiliated with pyrosulfate or bisulfate species. In conventionally prepared materials, the activity of zirconia depends critically on the ability to partly decompose and chemisorb SO_3 during calcination and thereby form active pyrosulfate groups. The direct chemisorption of SO_3 circumvents this step and opens so a wide area of surface modifications for oxides that has not been available to now.

Acknowledgments

Financial support from the Deutsche Forschungsgemeinschaft (DFG) in the framework of DFG priority program 1091, “Bridging the gap in Heterogeneous Catalysis,” is gratefully acknowledged. The authors are indebted to Dr. C. Breitkopf, Dr. S. Wrabetz, M. Standke, Dr. K. Meinel, and Dr. A. Hofmann, and thank Professor J. Sauer, Professor H. Papp, and Dr. F. Jentoft for valuable discussions.

References

[1] T. Yamaguchi, K. Tanabe, Y.C. Kung, Mater. Chem. Phys. 16 (1986) 67.
[2] J.R. Sohn, H.W. Kim, J. Mol. Catal. 52 (1989) 361.
[3] D. Fărcaşiu, J.Q. Li, Appl. Catal. A 175 (1998) 1.
[4] M.T. Tran, N.S. Gnep, G. Szabo, M. Guisnet, Appl. Catal. A: Gen. 171 (1998) 207.
[5] M. Hino, S. Kobayashi, K. Arata, J. Am. Chem. Soc. 101 (1979) 6439.
[6] R.A. Comelli, C.R. Vera, J.M. Parera, J. Catal. 151 (1995) 96.
[7] C. Morterra, G. Cerrato, F. Pinna, M. Signoretto, J. Catal. 157 (1995) 109.
[8] D. Fărcaşiu, J.Q. Li, Appl. Catal. A: Gen. 128 (1995) 97.
[9] F. Lonyi, J. Valyon, J. Engelhardt, F. Mizukami, J. Catal. 160 (1996) 279.
[10] C. Morterra, G. Cerrato, M. Signoretto, Catal. Lett. 41 (1996) 101.
[11] C. Morterra, G. Cerrato, G. Meligrana, M. Signoretto, F. Pinna, G. Strukul, Catal. Lett. 73 (2001) 113.
[12] W. Stichert, F. Schüth, J. Catal. 174 (1998) 242.
[13] C.R. Vera, J.M. Parera, J. Catal. 165 (1997) 254.
[14] A.F. Bedilo, A.S. Ivanova, N.A. Pakhomov, A.M. Volodin, J. Mol. Catal. A: Chem. 158 (2000) 409.
[15] T. Yamaguchi, T. Jin, K. Tanabe, J. Phys. Chem. 90 (1986) 3148.
[16] J.F. Haw, J. Zhang, K. Shimizu, T.N. Venkatraman, D.P. Luigi, W. Song, D.H. Barich, J.B. Nicholas, J. Am. Chem. Soc. 122 (2000) 12561.
[17] J. Zhang, J.B. Nicholas, J.F. Haw, Angew. Chem. Int. Ed. 39 (2000) 3302.
[18] P. Canton, R. Olindo, F. Pinna, G. Strukul, P. Riello, M. Meneghetti, G. Cerrato, C. Morterra, A. Benedetti, Chem. Mater. 13 (2001) 1634.
[19] X. Li, K. Nagaoka, J.A. Lercher, J. Catal. 227 (2004) 130.
[20] N. Katada, J. Endo, K. Notsu, N. Yasunobu, N. Naito, M. Niwa, J. Phys. Chem. B 104 (2000) 10321.
[21] W. Hertl, Langmuir 5 (1989) 96.
[22] A.A. Tsyganenko, V.N. Filimonov, J. Mol. Struct. 19 (1973) 579.
[23] T. Yamaguchi, T. Jin, K. Tanabe, J. Phys. Chem. 90 (1986) 3148.
[24] M. Waqif, J. Bachelier, O. Saur, J.C. Lavalley, J. Mol. Catal. 72 (1992) 127.
[25] C.A. Emeis, J. Catal. 141 (1993) 347.
[26] X. Li, K. Nagaoka, L.J. Simon, R. Olindo, J.A. Lercher, A. Hofmann, J. Sauer, J. Am. Chem. Soc., in press.
[27] X. Li, K. Nagaoka, L.J. Simon, R. Olindo, J.A. Lercher, J. Catal. 232 (2005) 456.
[28] X. Li, K. Nagaoka, L.J. Simon, R. Olindo, J.A. Lercher, in preparation.
[29] K. Arata, Adv. Catal. 37 (1990) 165.
[30] A. Clearfield, G.P.D. Serrette, A.H. Khazi-Syed, Catal. Today 20 (1994) 295.
[31] C. Morterra, G. Cerrato, C. Emanuel, C. Bolis, J. Catal. 142 (1993) 349.
[32] A. Hofmann, J. Sauer, J. Phys. Chem. B 108 (2004) 14652.
[33] L.M. Kustov, V.B. Kazansky, F. Figueras, D. Tichit, J. Catal. 150 (1994) 143.
[34] V. Adeeva, J.W. de Haan, J. Janchen, G.D. Lei, V. Schunemann, L.J.M. van de Ven, W.M.H. Sachtler, R.A. van Santen, J. Catal. 151 (1995) 364.
[35] T. Yamaguchi, K. Tanabe, Mater. Chem. Phys. 16 (1986) 67.