Acidity of sulfated zirconia as studied by FTIR spectroscopy of adsorbed CO and NH_3 as probe molecules

D. Spielbauer, G.A.H. Mekhemer [1], M.I. Zaki [2] and H. Knözinger [3]

Institut für Physikalische Chemie, Universität München, Sophienstrasse 11, 80333 Munich, Germany

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The acid properties of pure and sulfated zirconias were studied by FTIR spectroscopy of adsorbed CO and NH_3 as probe molecules. Whereas pure monoclinic zirconia shows only Lewis acidity, sulfation of tetragonal and monoclinic zirconia creates new bridging OH groups. Two types of Brønsted-acidic centers and two types of Lewis-acidic centers with enhanced acid strength were identified. A communication between the different types of Lewis-acidic sites and the related adsorbed sulfate molecules could be shown. The coordination of basic molecules such as CO onto Lewis-acid sites induces a decrease of the intrinsic Brønsted-acidity of the bridging OH groups. These effects are discussed on the basis of a model of the acidic centers that was previously proposed.

Keywords: zirconia-sulfated; Lewis acidity; Brønsted acidity; FTIR spectroscopy; probe molecules; CO; NH_3

1. Introduction

Sulfated zirconia has been proposed as a strong solid acid catalyst for the isomerization of *n*-butane to isobutane [1], which is of industrial interest as a reactant for the production of isooctane and methyl tert-butyl ether (MTBE) [2]. The isomerization of *n*-butane is usually assumed to proceed via carbocations [3]. Assuming a monomolecular transformation of a secondary carbocation into a tertiary carbocation with cyclopropyl intermediates [4], the isomerization of *n*-butane would require very strong acids or superacids, since primary carbocations would be involved as intermediates. However, recent measurements of the acidity of sulfated zirconia indicated the presence of strong acid centers, which were weaker than the strong acid sites of zeolites such as HZSM-5 [5,6]. Therefore, based on ^{13}C-labelling experiments, a bimolecular mechanism via C_8^+ ions was proposed, which does not require primary carbocations [7,8].

Various model structures for the adsorbed sulfate groups were proposed in the literature. These include doubly bonded structures with two S=O groups [9,10], and triply bonded structures that contain only one S=O group [11]. Bisulfate-like doubly bonded structures were also discussed [12] as possible surface species. Recently, White et al. [13] proposed a pentacoordinated model sulfate species with four anchoring bonds to the [001]-surface plane of tetragonal ZrO_2. However, the reported vibration frequencies do not, in our opinion, unequivocally support this structure. Based on results from Raman and FTIR spectroscopy and ^1H-MAS-NMR, Riemer et al. [14] presented a model sulfate structure having two anchoring bonds to the ZrO_2 surface, one S=O group and one bridging OH that was thought to form a coordination bond to a Zr^{4+} Lewis-acid center. The resulting strong polarization of the O–H bond was considered to create the strong Brønsted acidity. Others – based on the different model structures – have favoured different origins for the acid properties of the sulfated zirconias. The chemisorption of water molecules has been proposed to create protonic acid centers [9,10] in connection with doubly bridging structures, or to hydrolyse the triply bridging structure with formation of SOH groups [11].

The common procedure of producing sulfated zirconia catalysts is the sulfation of the hydroxide of zirconia. This precursor crystallizes in the tetragonal ZrO_2 phase (t-ZrO_2) and shows high activity for the alkane isomerization [15–17]. In contrast, materials obtained by sulfation of crystallized monoclinic ZrO_2 (m-ZrO_2) show no or only low catalytic activity [14,16,17]. From these results it was concluded, that amorphous zirconium hydroxides are needed for the creation of strong acid sites [16]. The reason for these structural requirement is, however, not well understood as yet.

The aim of the present paper is (i) the characterization of the acidity of pure monoclinic zirconia and sulfated monoclinic and tetragonal zirconia by FTIR spectroscopy using CO and ammonia as probe molecules; (ii) the development of a model of the acidic sites and for the generation of acidity based on the structures of the adsorbed sulfate molecules; and (iii) a critical discussion of the characterization of the acidity of sulfated zirconia by probe molecules.

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[1] To whom correspondence should be addressed.

[2] On leave from Department of Chemistry, Faculty of Science, Minia University, El-Minia, Egypt.

[3] Department of Chemistry, Kuwait University, Kuwait.

2. Experimental

The materials $Zr(OH)_4$ type XZO 632/3 and $Zr(OH)_4/(NH_4)_2SO_4$ (6–7.2 wt% SO_4) type XZO 682/1, dried at 393 K, were obtained from MEL, Manchester (England). Pure zirconia was prepared by calcination of $Zr(OH)_4$ at 873 K for 1 h. It is designated as Zr(873). The sulfated $Zr(OH)_4$ was calcined in the same way at $T_2 = 773$–973 K to obtain samples Zr(393)S(T_2). An additional set of samples was prepared by sulfation of a monoclinic ZrO_2, which was obtained by calcination of the $Zr(OH)_4$ at 873 K for 4 h and which had a specific surface area of 35 m^2/g. The material was suspended in an aqueous solution of $(NH_4)_2SO_4$ for 1 h and subsequently dried by evaporation of the water. The dried sulfated material contained nominally 7.2 wt% SO_4. After calcination at $T_2 = 773$–973 K samples were obtained, which are designated Zr(873)S(T_2).

The experimental studies in the present paper will concentrate on the pure monoclinic zirconia Zr(873), the sulfated monoclinic zirconia Zr(873)S(873), and on the sulfated tetragonal zirconia Zr(393)S(873). The specific surface areas measured by the BET method, the crystallographic phase compositions, as calculated from XRD patterns by the method of Toraya et al. [18], and the sulfate contents of the calcined samples, measured by the LECO method as SO_2, are summarized in table 1. Corresponding to the different specific surface areas of the zirconia precursors, the sulfated monoclinic zirconia shows an enhanced loss of sulfate during the calcination step as compared to the sulfated $Zr(OH)_4$. It must be emphasized, that no bands of uncoordinated sulfate or crystalline $(NH_4)_2SO_4$ were obtained in the Raman and the IR spectra of the samples Zr(393)S(873) and Zr(873)S(873) [14]. The catalytic activities of the samples were previously tested by the isomerization of *n*-butane to isobutane in the temperature range 393–473 K with He as a carrier gas [19]. Whereas the sample Zr(393)S(873) showed a high conversion, the activity of Zr(873)S(873) was only very low and the unsulfated material Zr(873) was totally inactive.

The IR spectra were recorded with a Bruker IFS-88 FT-IR spectrometer equipped with a liquid-nitrogen cooled MCT detector. A specially designed transmission cell, which was described in detail elsewhere [20], allows in situ pretreatment at temperatures up to 770 K and permits to record spectra between 80 and 300 K in vacuo ($\leqslant 10^{-5}$ mbar) or in a static gas atmosphere. The samples were prepared as thin self-supporting wafers (typically ca. 20 mg/cm^2). These specimens were pretreated in situ by calcination at 723 K in O_2 for 1 h and subsequent evacuation at 723 K for 1 h. The spectra were recorded with a spectral resolution of 2 cm^{-1}. CO ($\geqslant$99.997%, Linde AG) and NH_3 ($\geqslant$99.98%, Linde AG) were used as probe molecules. CO was further purified by passing it through an Oxisorb cartridge.

Table 1
Surface area, phase composition and sulfate content of Zr(873), Zr(873)S(873) and Zr(393)S(873)

	S_{BET} (m^2/g)	t-/m-ZrO_2	SO_4 (wt%)
Zr(873)	85	4 : 96	–
Zr(873)S(873)	32	8 : 92	2.7
Zr(393)S(873)	100	95 : 5	5.9

3. Results and discussion

3.1. *Adsorption of carbon monoxide*

3.1.1. *Hydroxyl stretching region (3300–3900 cm^{-1})*

Adsorption of CO was carried out at 77 K by a stepwise increase of the CO pressure from 0.5 to 40 mbar. Spectra were recorded at 77 K.

In the IR spectrum of pure zirconia Zr(873), three OH bands at 3780, 3740 (w) and 3680 cm^{-1} are observed prior to adsorption of CO (spectrum a in fig. 1A). Whereas the bands at 3780 and 3680 cm^{-1} are typical for m-ZrO_2 [21], the weak band at 3740 cm^{-1} is probably caused by silica [22], which is present as an impurity in the used pure and sulfated $Zr(OH)_4$. Addition of CO induces a shift of the band of the acidic OH groups at 3680 cm^{-1} to 3610 cm^{-1} (spectra b–i in fig. 1A). The other two bands of basic OH groups are not affected by CO adsorption.

For the sulfated m-ZrO_2 Zr(873)S(873), a new OH band at 3640 cm^{-1} appears while the characteristic OH bands of m-ZrO_2 have essentially disappeared (spectrum a in fig. 1B). Adsorption of CO results in a decrease of the band at 3640 cm^{-1}. Simultaneously the increase of two new bands at 3480 and 3420 cm^{-1} was observed (spectra b and c in fig. 1B). At higher pressures of CO (> 5 mbar) (spectra d–i in fig. 1B) the band at 3420 cm^{-1} is superimposed by a band at 3480 cm^{-1}. Very similar spectra were obtained for the sulfated t-ZrO_2 Zr(393)S(873) (fig. 1C). Two different acidic types of OH groups were also detected by ^{1}H-MAS-NMR spectroscopy [23].

Sulfation of m-ZrO_2 (Zr(873)S(873)) causes new OH groups, with an OH stretching frequency typical for bridging OH groups. Adsorption of CO results in a larger shift of the OH band which is indicative for a more acidic character of these OH groups as compared to the OH groups of pure m-ZrO_2. The absence of the band of basic OH groups of m-ZrO_2 at 3780 cm^{-1} after sulfation of m-ZrO_2 suggests, that the adsorption of sulfates on m-ZrO_2 proceeds by substitution of these basic OH groups. Very similar IR spectra were obtained for sulfated t-ZrO_2 Zr(393)S(873) (without and with adsorbed CO) despite their different crystalline structure. The Raman and IR spectra of both types of sulfated ZrO_2 show very similar spectral features in the SO stretching region which could be attributed to triply bridging sulfate molecules. According to these results and the nearly

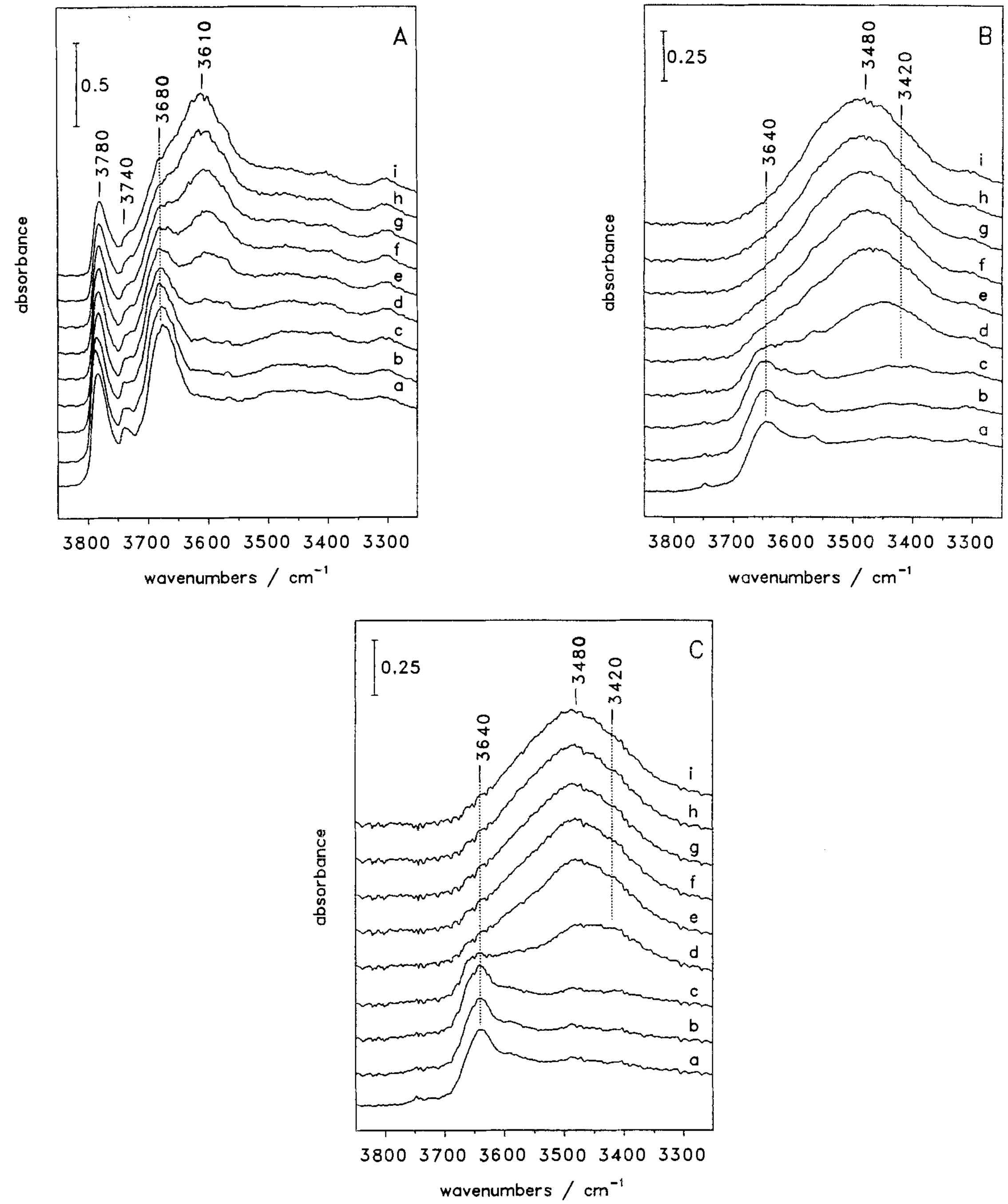
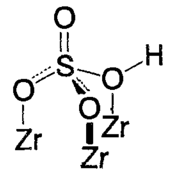


Fig. 1. IR spectra of the hydroxyl region (a) before and after the adsorption of (b) 0.5, (c) 1.0, (d) 3.0, (e) 5.0, (f) 10.0, (g) 20.0, (h) 30.0, and (i) 40.0 mbar CO at 77 K measured at 77 K. (A) Zr(873); (B) Zr(873)S(873); (C) Zr(393)S(873).

identical frequencies of the new OH groups for both types of sulfated ZrO_2, a model of the Brønsted-acidic centers with a dative bond of a sulfate OH group to Zr^{4+} was proposed [14] (structure 1). The enhancement of the Brønsted acidity of the bridging OH group is induced by the strong Lewis-acidic Zr^{4+} center (vide infra).

3.1.2. Carbonyl stretching region (2100–2250 cm^{-1})

The spectra in the CO stretching region were obtained by subtracting the (background) spectra of the CO-free samples and the gas phase spectra from the spectra of the samples with adsorbed CO. After adsorption of 0.5 mbar CO on pure m-ZrO_2 Zr(873) (spectrum a in fig. 2A) a band at 2188 cm^{-1} was observed, which is characteristic for CO coordinated to Lewis-acidic centers (Zr^{4+}) via an



Structure 1. Model of adsorbed sulfate molecules on zirconia and the protonic centers.

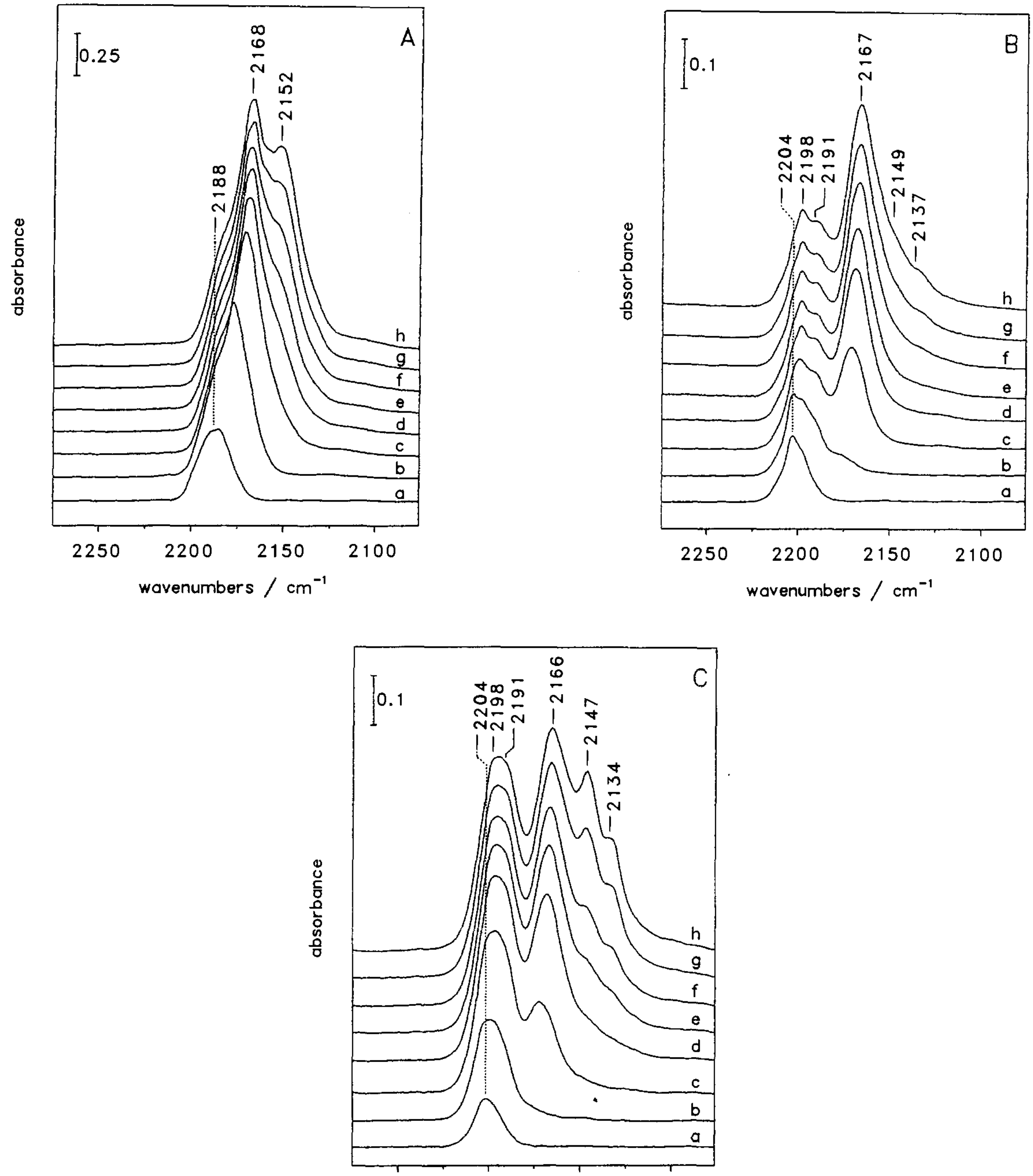


Fig. 2. IR spectra of the carbonyl region after the adsorption of (a) 0.5, (b) 1.0, (c) 3.0, (d) 5.0, (e) 10.0, (f) 20.0, (g) 30.0, and (h) 40.0 mbar CO at 77 K measured at 77 K (CO region). (A) Zr(873); (B) Zr(873)S(873); (C) Zr(393)S(873).

interaction of the non-bonding 5σ orbital of CO with the empty d orbitals of Zr^{4+}. At a pressure of 1.0 mbar CO (spectrum b in fig. 2B), the band was shifted to lower wavenumbers by an inductive effect caused by neighbouring CO molecules, which is characteristic of the semiconducting oxides such as TiO_2, ZrO_2 and HfO_2 [24]. An additional band at 2177 cm^{-1} (spectrum b in fig. 2A), caused by CO adsorbed on OH groups [25,26], is shifted to 2168 cm^{-1} at higher pressures of CO (spectra b–h in fig. 2A). A band at 2152 cm^{-1} at highest pressures of CO (40 mbar) (spectrum h in fig. 2A) is indicative of physisorbed CO.

For the sulfated m-ZrO_2 Zr(873)S(873), a band at 2204 cm^{-1} typical for CO adsorbed on Zr^{4+} centers was observed at a pressure of 0.5 mbar CO (spectrum b in fig. 2B). Increasing pressure of CO caused a shift of the band to 2198 cm^{-1} by inductive effects, and the formation of an additional band at 2191 cm^{-1} of CO adsorbed on Zr^{4+} centers (spectra b–h in fig. 2B). The intensity of a shoulder at 2177 cm^{-1} for CO H-bonded to OH groups at a pressure of 1.0 mbar (spectrum b in fig. 2B) increases and shifts to 2167 cm^{-1} with increasing pressures of CO (spectra c–h in fig. 2B). Shoulders at 2149 and 2137 cm^{-1} are caused by physisorbed CO (spectrum h in fig. 2B).

Whereas the carbonyl frequencies observed for CO adsorbed on sulfated t-ZrO_2 Zr(393)S(873) (fig. 2C) and sulfated m-ZrO_2 Zr(873)S(873) (fig. 2B) are very similar, the relative intensities of the bands at 2204 and 2191 cm^{-1} for CO on Zr^{4+} centers and of the bands for CO H-bonded to OH groups are different. The increased widths of the carbonyl bands for sulfated t-ZrO_2 are probably the result of an enhanced heterogeneity of the surface of this sample as indicated by XRD and Raman data of this material.

Sulfated m-ZrO_2 shows an increased Lewis-acid strength as compared to pure m-ZrO_2. At least two different types of Lewis-acid centers were observed (bands at 2204 and 2191 cm^{-1}). Pure m-ZrO_2 as well as the sulfated material show a shift of the stretching band of CO adsorbed on Zr^{4+} centers to lower wavenumbers already at low coverages of CO. This inductive effect will be discussed in more detail in the next section. For the sulfated tetragonal sample Zr(393)S(873), the same frequencies for CO adsorbed on Zr^{4+} centers were observed. Consequently, the sulfation of t- and m-ZrO_2 causes the same enhancement of the Lewis-acid strength. The differences in the relative intensities of the bands for CO coordinated to Zr^{4+} centers and H-bonded to OH groups suggest an increased number of Lewis-acid sites for sulfated t-ZrO_2. This fact might be related to the higher activity of sulfated t-ZrO_2 for the isomerization of *n*-butane to isobutane as compared to sulfated m-ZrO_2. According to the proposed model for the acidic centers on the surface of sulfated ZrO_2, the Lewis-acid strength of the Zr^{4+} ions would be increased by the electron accepting character of sulfate. Carbonyl band positions at somewhat higher frequencies were reported when CO was adsorbed at very low pressures (ca. 10^{-2} mbar), on sulfated zirconia ex hydroxide [27] or ex zirconium sulfate [28].

3.1.3. Sulfate region (1200–1500 cm^{-1})

In the IR spectrum of the sulfated m-ZrO_2 Zr(873)S(873), two bands at 1395 and 1402 cm^{-1} are observed in the absence of CO (spectrum a in fig. 3A). These bands are attributed to free S=O groups of triply coordinated sulfate species with slightly different bond orders and/or geometries [29]. After the adsorption of CO at a pressure of 0.5 mbar both SO bands are shifted to lower wavenumbers by a about 10 cm^{-1} (spectrum b of fig. 3A). This effect was also reported by Pinna et al. [30] for sulfated ZrO_2 and by Lange et al. [31] for sulfated TiO_2. Comparing the related spectral feature in the CO region shows that only bands of CO adsorbed on Lewis-acidic centers (Zr^{4+}) are observed at these low coverages (spectrum a in fig. 2B). Increasing the pressure and the coverage of CO causes the adsorption on Zr^{4+} centers and in addition on OH groups and a further shift of the SO bands to 1383 and 1368 cm^{-1}, respectively, (spectra c–i in fig. 3A) is observed. The differences between successive spectra show clearly, that especially the adsorption of CO on Lewis-acid sites causes a shift of the SO bands (spectra b and c in fig. 3B).

The sulfated t-ZrO_2 Zr(393)S(873) shows an asymmetric band at 1402 cm^{-1} of free S=O groups of adsorbed sulfate molecules in the absence of CO (spectrum a in fig. 3C). Adsorption of CO causes a shift of this band to lower wavenumbers as described above. The final position of the band at a pressure of 40 mbar CO is 1386 cm^{-1} with a shoulder at 1369 cm^{-1} (spectra b–i in fig. 3C). It is noteworthy, that this shoulder could not be resolved in the spectrum in the absence of CO. The same effect was observed for the sample Zr(873)S(873), where the splitting between the two SO bands increases by the adsorption of CO from $(1402-1395=)7$ cm^{-1} to $(1383-1368=)15$ cm^{-1}. Considering the difference spectra, shows again that predominantly the adsorption of CO on Zr^{4+} centers causes the shift of the SO bands (spectra b and c in fig. 3D).

As the frequencies of S–O bands are clearly correlated with their bond order [29], a shift of the S=O band of adsorbed sulfate molecules to lower wavenumbers indicates a lowering of the bond-order for the free S=O group caused by an increasing bond-order of the bridging S–O groups (structure 2). According to the proposed model of the acidic centers of sulfated zirconia (structure 1), a higher electron density at the bridging O atoms probably causes a weakening of the bridging OH group. This should affect the measurement of the Brønsted acidity of the material by adsorption of probe molecules such as CO, acetonitrile or other basic molecules. A comparison in table 2 of the shifts of the OH bands by adsorption of CO under saturation conditions for sulfated zirconia with those of other strong Brønsted-acidic materials such as HZSM-5 [26,32] or H-mordenite [32] suggests, that the sulfated zirconia is a weaker Brønsted acid than the acidic zeolites. Similar results were obtained by ^{1}H-MAS-NMR spectroscopy with acetonitrile as a probe molecule [6]. These basic probe molecules are initially adsorbed on Lewis-acid centers which causes a weakening of the Brønsted acidity of the bridging OH groups prior to their interaction with the probe molecule. The observed shift of the OH band induced by the adsorption of CO molecules and the related virtual Brønsted acidity of the OH groups is therefore lower than the intrinsic acidity of the material.

The splitting of the SO band and the band for CO adsorbed on coordinatively unsaturated (cus) Zr^{4+} indicates different types of species. Fig. 4 shows the carbonyl stretching and the sulfate region of the IR spectra of different samples of sulfated zirconia. After the adsorption of CO one recognizes two bands in the carbonyl stretching region for CO adsorbed on cus Zr^{4+} at 2196–2199

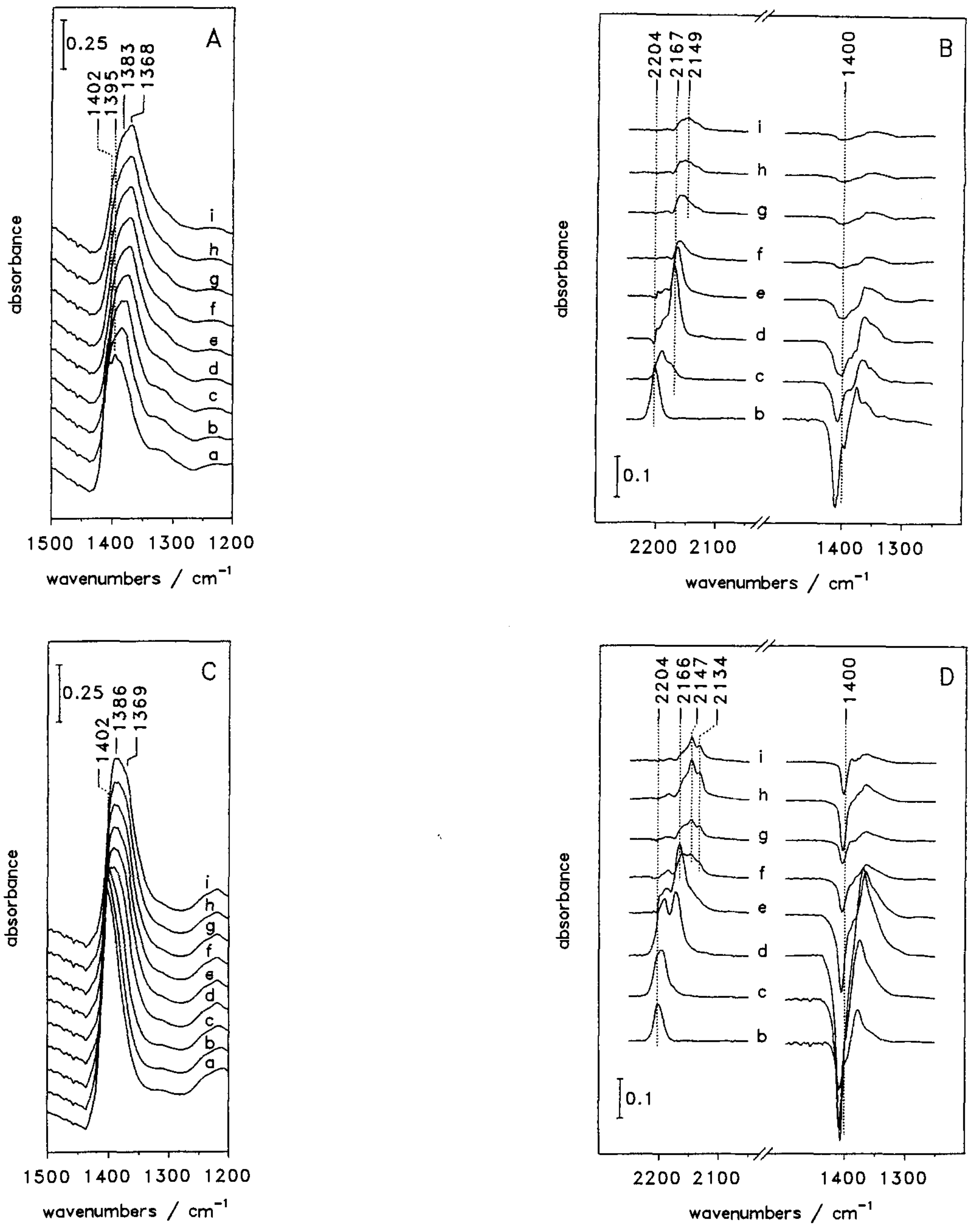
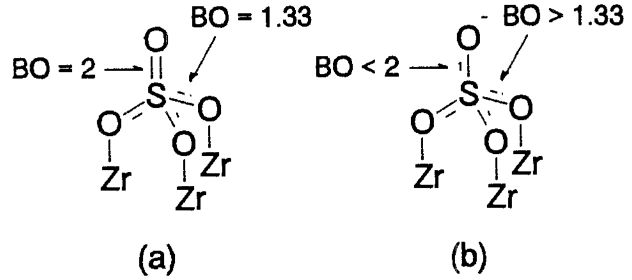


Fig. 3. IR spectra (SO region) and difference spectra (CO region and SO region) (a) before and after the adsorption of (b) 0.5, (c) 1.0, (d) 3.0, (e) 5.0, (f) 10.0, (g) 20.0, (h) 30.0, and (i) 40.0 mbar CO at 77 K measured at 77 K. (A) Zr(873)S(873); (B) Zr(873)S(873) (difference spectra); (C) Zr(393)S(873); (D) Zr(393)S(873) (difference spectra).

and at 2190–2191 cm^{-1} as discussed above (in the case of the sample Zr(393)S(773), spectrum a in fig. 4B, these two bands could not be resolved). In the sulfate region two bands at 1381–1386 and at 1365–1372 cm^{-1} are observed for the free S=O group of adsorbed sulfate molecules after the adsorption of CO (solid lines). The intensities of the lower frequency band in the carbonyl stretching and in the sulfate region seem to increase with calcination temperature T_2 relative to the corresponding higher frequency bands. This means that there are two types of sulfate species which cause different Lewis-acid strength for the related cus Zr^{4+}. The more acidic species is the dominant one for the samples Zr(393)S(773,873) (spectra a and b in fig. 4B), whereas the less acidic species dominates for all other samples. In spite of this effect, it is noteworthy that the intensity ratios between the related bands are very similar. This is also in agreement with the two different acidic types of OH groups, observed by IR spectroscopy in the present work and by ^{1}H-MAS-NMR spectroscopy [23].

As discussed above, the adsorption of CO on pure ZrO$_2$ causes a shift of the band for CO on cus Zr^{4+} by an inductive effect even at very low coverages of CO. For the sulfated samples a similar but less pronounced effect



Structure 2. Model of the change of bond order of the S=O bond for the adsorbed sulfate molecules.

was observed, whereas for these materials the bands of the free S=O groups show significant shifts to lower wavenumbers. Consequently the adsorbed sulfate molecules seem to partially compensate the inductive effect by neighbouring CO molecules.

3.2. *Adsorption of ammonia*

NH_3 was adsorbed on the samples at room temperature (RT) at pressures up to 15 mbar. Spectra of adsorbed NH_3 were recorded at RT after a subsequent evacuation at RT for 15 min. After adsorption of NH_3 on pure zirconia Zr(873), bands at 1603, 1193 and 1170 cm^{-1} were observed (spectrum a in fig. 5). The band at 1603 cm^{-1} is characteristic for the antisymmetric deformation vibration (δ_{as}) of NH_3 adsorbed on Lewis-acidic centers (cus Zr^{4+}) [33]. The appearance of two symmetric deformation vibrations (δ_s) of such complexes at 1193 and 1170 cm^{-1} indicates the presence of two different types of Lewis-acidic centers. Since no bands for NH_4^+ were observed, the pure zirconia has no Brønsted-acidic centers in agreement with literature data [34].

The sulfated m-ZrO_2 Zr(873)S(873) (spectrum b in fig. 5) shows new bands at 1610, 1273 and 1250 (sh) cm^{-1} which are to be attributed to NH_3 coordinated to cus Zr^{4+}. Additional bands at 1680 (vw), 1483 and 1448 cm^{-1} are typical for the δ_{as} and δ_s vibrations of adsorbed NH_4^+ [33], created by proton transfer from the OH groups to NH_3. The number of δ_s vibrations is indicative for the presence two different Brønsted-acidic centers, as already concluded from the results of the CO adsorption. The shift of the bands for the δ_s vibration of NH_3 coordinated to cus Zr^{4+} as compared to pure m-ZrO_2 is indicative for an increased Lewis-acid strength in agreement with the results of the experiments with CO.

Table 2
$\tilde{\nu}_{OH}$ and $\Delta\tilde{\nu}_{OH-CO}$ under saturation conditions for pure zirconia, sulfated zirconia and acidic zeolites

	$\tilde{\nu}_{OH}$ (cm^{-1})	$\Delta\tilde{\nu}_{OH-CO}$ (cm^{-1})	Ref.
m-ZrO_2	3780	–	this work
	3680	70	
ZrO_2/SO_4	3640	160	this work
		220	
H-ZSM-5	3670	220	[26,32]
	3620	340	
mordenite	3620	290	[32]

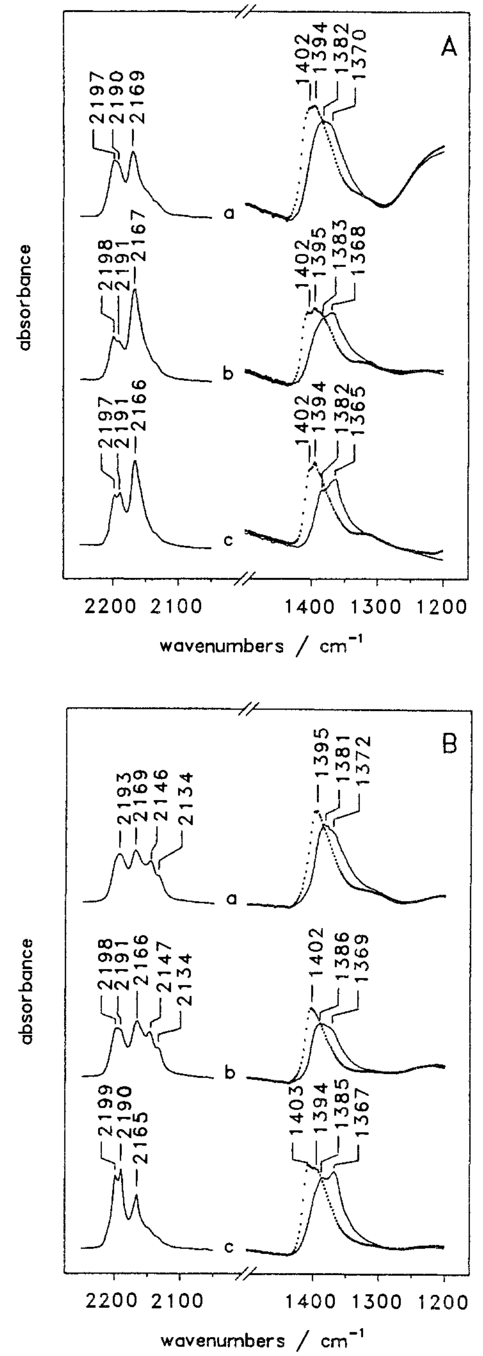


Fig. 4. IR spectra before (dotted lines) and after (solid lines) the adsorption of 40 mbar CO at 77 K measured at 77 K (CO region, SO region). (A) Zr(873)S(T_2); (B) Zr(393)S(T_2); (a) T_2 = 773, (b) 873 and (c) 973 K (intensities in CO region expanded by a factor 2).

For the sulfated t-ZrO_2 Zr(393)S(873) (spectrum c in fig. 5), similar bands are observed at 1610, 1279 and 1248 (sh) cm^{-1} for NH_3 coordinated to cus Zr^{4+}, and bands at 1680, 1483 and 1448 cm^{-1} for NH_4^+ formed by proton transfer from OH groups to NH_3.

The adsorption of NH_3 clearly demonstrates, that

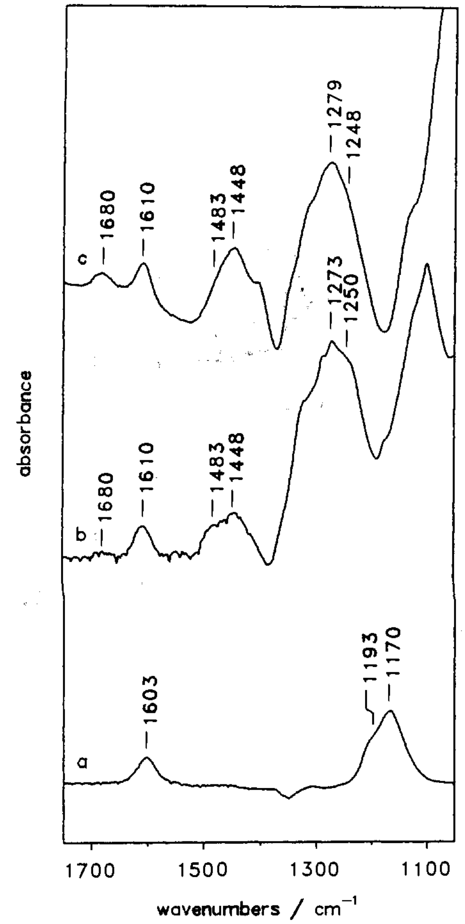


Fig. 5. IR spectra after the adsorption of 15 mbar NH_3 at RT and subsequent evacuation at RT for 15 min measured at RT (NH region) (a) Zr(873), (b) Zr(873)S(873), and (c) Zr(393)S(873).

the sulfation of zirconia creates two different types of Brønsted-acidic centers and two different types of Lewis-acidic centers (cus Zr^{4+}) in agreement with the results of the CO experiments. No differences were found between the monoclinic and the tetragonal zirconia as regards the number of types of acid centers and their strengths.

After the adsorption of NH_3, the S=O band of the sulfated samples is broadened and shifted from ca. 1400 cm^{-1} to ca. 1290 cm^{-1}. The origin of this shift may have various reasons:

(i) an inductive effect by the adsorption of NH_3 at the Lewis-acidic centers (cus Zr^{4+}) while retaining the structures of the sulfates, as proposed for the adsorption of CO;

(ii) the transfer of a proton from the proposed acidic OH groups with formation of NH_4^+ and also retaining the structures of the sulfates:

$$[(Zr-O)_3S{=}O]H + NH_3 \rightarrow (Zr-O)_3SO^- NH_4^+ \qquad (1)$$

and/or

(iii) a dissociative adsorption of NH_3 by formation of an amine accompanied by a change of the structures of the sulfates, corresponding to a hydrolysis [31]:

$$(Zr-O)_3S{=}O + NH_3 \rightarrow (Zr-O)_2SO_2^- H^+ + Zr-NH_2 \qquad (2)$$

4. Conclusions

Sulfation of t- and m-ZrO_2 creates new OH groups with an OH-stretching frequency characteristic of bridging OH groups. Adsorption of basic probe molecules (CO and NH_3) indicates the formation of different types of strong Brønsted-acidic and Lewis-acidic sites. As the observed IR spectra of sulfated m-ZrO_2 and t-ZrO_2 are nearly identical in the OH regime in the presence and absence of adsorbed probe molecules, the new bridging OH groups are presumably connected with the sulfates (see structure 1).

The position of the S=O band has proved to be very sensitive to changes of the electron densities by the adsorption of basic molecules to Lewis-acidic sites (cus Zr^{4+}) at the surface. In this way a communication between different types of Lewis-acidic sites and the related adsorbed sulfate molecules could be shown. Corresponding to the suggested model for the acidic centers of sulfated zirconia the adsorption of basic molecules at Lewis-acidic sites probably causes a decrease of the intrinsic Brønsted acidity of the bridging OH groups. As the initial adsorption of basic molecules such as CO proceeds at the Lewis-acidic sites, such basic molecules must necessarily lead to a modification of the Brønsted acidity of sulfated zirconia. This effect is possibly the origin of the observed differences between the activity for the acid catalyzed isomerization of *n*-butane and the Brønsted acidity as detected by adsorbed probe molecules, of sulfated zirconia and other strong acidic materials such as HZSM-5. Nevertheless, a correlation between the type of acidity and the catalytic activity of sulfated zirconia is not yet possible on the basis of the presented spectroscopic data.

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