JOURNAL OF CATALYSIS **150**, 143–149 (1994)

Investigation of the Acidic Properties of ZrO_2 Modified by SO_4^{2-} Anions

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Received August 24, 1993; revised June 1, 1994

Zirconium dioxide modified by sulfate anions was investigated using diffuse reflectance IR spectroscopy. It was found that this modification enhanced the strength of both Brønsted acid sites (terminal or bridging ZrOH groups) and Lewis acid sites (low-coordinate Zr ions). However, Brønsted acid sites with enhanced strength appeared to be weaker than bridging OH groups in zeolites. Modification also created protons with a new environment. These protons were assumed to form multicenter bonds with oxygen atoms of SO_4^{2-} anions or with neighboring basic oxygen and to possess acidic properties comparable to those of protons in zeolites. Low-temperature ethylene and cyclopropane oligomerization and H–D exchange were shown to proceed on sulfated zirconia, presumably with participation of such sites.

INTRODUCTION

The recent breakthrough in the chemistry of and catalysis by nonzeolitic solid superacids is related, in particular, to the problem of activation and utilization of paraffins as well as to new applications of superacids for the production of fine chemicals. In this respect metal oxides (ZrO_2, Fe_2O_3, TiO_2, SnO_2, etc.) modified by sulfate anions (1–7) have been shown to be the most promising superacidic catalysts for the low-temperature processes of isomerization, alkylation, and cracking of paraffins (8, 9). Brønsted acid sites are assumed to play a decisive role in these reactions. Their strength has often been determined by titration in the presence of Hammett indicators (1). The existence of both Brønsted and Lewis acid sites on sulfated catalysts has also been confirmed by IR spectra of adsorbed pyridine (10). However, the information about the nature and particular properties of acid centers of different types is rather limited, probably because of their low concentration. For instance, there are no direct IR-spectroscopic data on the influence of modification by sulfates on the properties of surface OH groups and Lewis acid centers.

In the present work these points have been investigated in detail by the highly sensitive method of diffuse reflectance IR spectroscopy using adsorption of various molecular probes.

EXPERIMENTAL

Different $Zr(OH)_4$ compounds were obtained in aqueous media by hydrolysis of $ZrOCl_2 \cdot 8H_2O$ or $ZrONO_3 \cdot xH_2O$ salt solutions (0.4 *M*) with adjusted quantities of NH_4OH (6 *M*). The precipitates obtained were stirred for 12 h at ambient temperature, filtered, and washed with hot deionized water (340–360 K) to remove excess salts ($AgNO_3$ or $(NH_4)_2SO_4$ tests). One sample was predried in vacuum at room temperature, but the products were usually dried at 383 K in air for 24 h.

The sulfated compounds were obtained by impregnation of the dried supports prepared as previously described, with 1 M H_2SO_4 solution (15 or 35 ml/g support) and further dried at 383 K for 24 h.

Two samples of SO_4^{2-}/ZrO_2 were prepared with different surface areas of 150 and 290 m^2/g (sample predried in vacuum) and SO_4^{2-} content of 5 wt%. For comparison, a commercial sample of ZrO_2 (surface area about 5 m^2/g) modified by H_2SO_4 treatment (5 wt% of SO_4^{2-} ions) was also studied. After modification all the samples were dried at 470 K for 5 h.

Before the spectroscopic measurements the samples were heated at 770–920 K in vacuum for 5 h. The rate of temperature increase was 5 K/min. Diffuse reflectance IR spectra were measured in the spectral range of 1300–400 cm^{-1} using a Perkin-Elmer 580B spectrometer and in the range of 4000–8000 cm^{-1} using Beckman Acta M-VII spectrophotometers equipped with the home-made diffuse reflectance attachments described previously (11, 12). For the 1300–4000 cm^{-1} range, glass vacuum cuvettes equipped with CaF_2 windows were used. For the near

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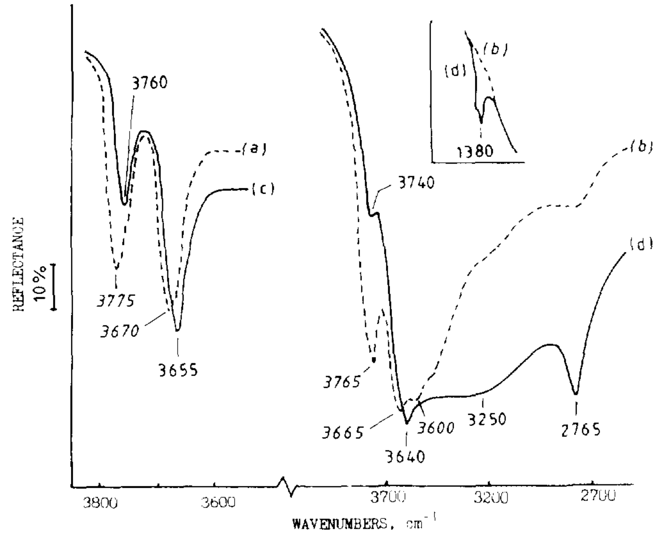


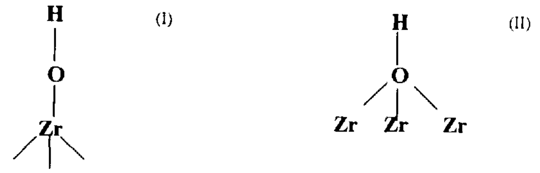
FIG. 1. IR spectra of parent (a, b) and modified (c, d) ZrO_2 heated at 770 K in vacuum for 5 h. (a) Nonmodified ZrO_2 (surface area = 5 m^2/g). (b) Nonmodified ZrO_2 (surface area = 290 m^2/g). (c) Samples (a) modified with 5% of SO_4 anions. (d) Sample (b) modified with 5% of SO_4 anions.

infrared, the cuvets were made from fused quartz. The samples were placed inside as powders. Adsorption of molecular hydrogen at 77 K, or CO, CH_4, C_2H_4, C_6H_{14}, C_6H_6, CD_3CN, C_2D_4, and cyclopropane at 300 K were used as molecular probes for identification of Brønsted and Lewis acid sites or for testing their reactivity.

RESULTS AND DISCUSSION

1. Brønsted Acidity

(a) *The nature of Brønsted acid sites.* Figure 1 shows the representative IR spectra of the parent ZrO_2 samples with surface areas 290 m^2/g and 5 m^2/g. In agreement with the literature data (14) they contain two types of isolated ZrOH groups which are characterized in the fundamental OH stretching region by the narrow IR bands at 3765–3770 cm^{-1} and 3665–3670 cm^{-1} (Fig. 1, spectra (a) and (b)). Note that the minima of reflectance in this spectrum and the following Figures correspond to maxima in absorption. An additional low frequency band at 3560 cm^{-1} appears in the spectra of the sample with a high surface area that may be attributed to weakly hydrogen-bonded OH groups of ZrO_2 or to another type of bridging OH groups. Their relative intensities are influenced by the surface area of the samples. The positions of the maxima of these bands are also slightly dependent on the surface area and pretreatment conditions. According to Ref. (14) these two lines may be attributed to terminal and bridging hydroxyls of the structures shown in Scheme 1. Also, low-intensity unresolved bands or shoulders at 3600 and 3500 cm^{-1}



SCHEME 1

could be observed, especially in the spectra of the samples with high surface areas. They may be attributed to hydrogen-bonded ZrOH groups.

For the sample with the high surface area of 290 m^2/g the corresponding three bands are also visible in the overtone part of the spectrum at 7015, 7180 and 7360 cm^{-1} (Fig. 2a), whereas for the low surface area sample they are too weak to be observed. The separation between the maxima of overtones is about twice as large as in the fundamental region. Therefore the resolution of the overtone spectra is better and the low frequency shoulder appears as a separate band at 7015 cm^{-1}.

In agreement with literature data the modification of ZrO_2 with SO_4^{2-} anions results in the appearance of a new IR band at 1380 cm^{-1} (Fig. 1d) which can be ascribed to the fundamental frequency of the asymmetric stretching vibrations (ν_{as} of SO_4^{2-} anions). We also succeeded in observing the corresponding first overtone band at 2765 cm^{-1} (Fig. 1d). The intensities of both bands correlate with the sulfur content in the samples and decrease after

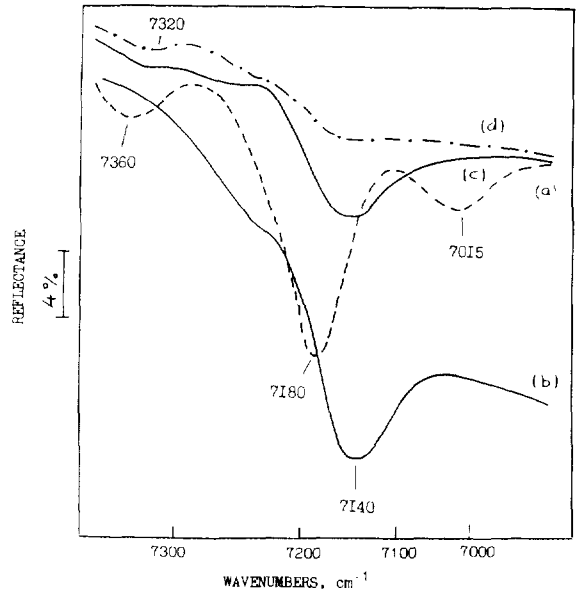


FIG. 2. First overtone IR spectra of parent and modified ZrO_2 samples heated at 770 K in vacuum for 5 h. (a) Nonmodified ZrO_2 (surface area = 290 m^2/g). (b) 5% SO_4^{2-}/ZrO_2 (surface area = 290 m^2/g). (c) 5% SO_4^{2-}/ZrO_2 (surface area = 150 m^2/g). (d) 5% SO_4^{2-}/ZrO_2 (surface area = 5 m^2/g).

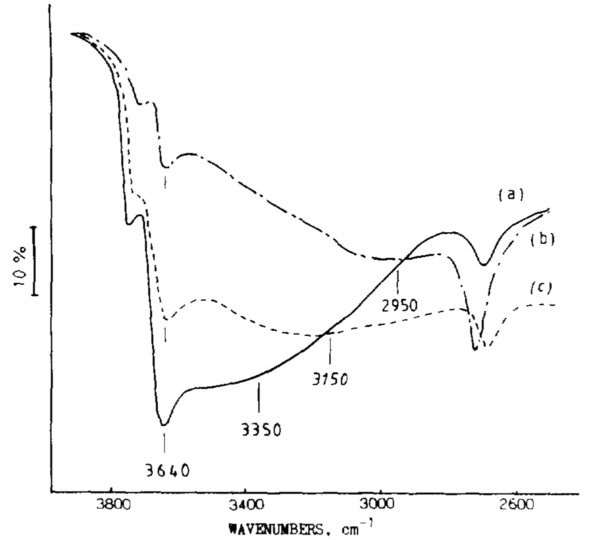
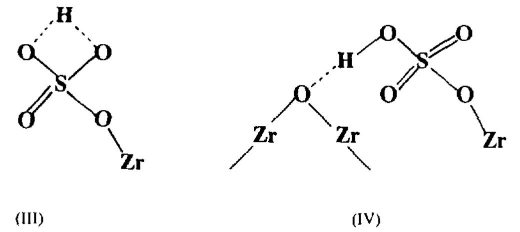


FIG. 3. IR spectra of 5% SO$_4^{2-}$/ZrO$_2$ (surface area = 290 m^2/g) heated at 770 K (a), 870 K (b), and 970 K (c) for 4 h.

prolonged high-temperature evacuation (at 870–920 K) because of the partial removal of sulfur.

In addition, the modification results in frequency shifts of the narrow bands at 3665 and 3670 cm^{-1} towards lower frequencies of 3655–3600 cm^{-1} and in the strong decrease of the high frequency 3765–3775 cm^{-1} line intensity (Figs. 1c, 1d). Both of these effects depend on the concentration of modifying SO$_4^{2-}$ ions and, perhaps, on the way of modification. Indeed, unlike modification using H$_2$SO$_4$, the treatment of zirconia and (NH$_4$)$_2$SO$_4$ results in weaker changes of the IR spectra.

The effects of modification are expressed even more clearly in the overtone region where only the single band at 7140 cm^{-1} with a very weak high frequency shoulder is observed (Fig. 2b). Thus the modification with sulfur anions eliminates the low and the high frequency bands and shifts the central band in the fundamental region about 25 cm^{-1} to lower frequency (about 40 cm^{-1} in the overtone region). It also results in the appearance of a very broad band with a maximum at 2950–3250 cm^{-1} (Fig. 3) depending on the concentration of sulfur and on the way of modification (H$_2$SO$_4$ or (NH$_4$)$_2$SO$_4$ treatment). Exchange of surface protons for deuterium by treatment with D$_2$O at 498 K results in its disappearance. Instead, a corresponding broad band appears in the region of O–D stretching vibrations below 2500 cm^{-1}, thus confirming the assignment of this broad band to acidic protons. This very broad band at 3250–2950 cm^{-1} can be attributed to protons resulting from the substitution of terminal ZrOH groups by HSO$_4^-$ anions. The structure of these sites may be represented by the following alternative ionic structure with a proton forming a multicenter bond with SO$_4^{2-}$ anion



SCHEME 2

or by a covalent structure with hydrogen-bonded hydroxyl, as in Scheme 2.

The thermal stability of the different types of OH groups in the samples under investigation is rather high. Both for unmodified and for sulfated zirconia the intensities of the bands of OH groups (ν = 3770–2950 cm^{-1}) start to decrease only after heating above 820 K (Fig. 3). Dehydroxylation proceeds the most drastically after calcination in a vacuum at 870–920 K. Simultaneously the broad band is shifted towards lower frequencies (from 3250 to 2950 cm^{-1} (Fig. 3), most probably because of the changes in the nearest surrounding of SO$_4^{2-}$ anions bearing multibonded protons.

(b) *Acidic properties of Brønsted sites.* The acidic properties and the reactivity of Brønsted acid sites in sulfated and parent ZrO$_2$ were estimated using the adsorption of weak bases like benzene and *in situ* reactions of oligomerization of ethylene or cyclopropane occurring directly in the IR cell after admission of reactant molecules at 300 K.

Figure 4 shows the IR-spectra appearing after adsorp-

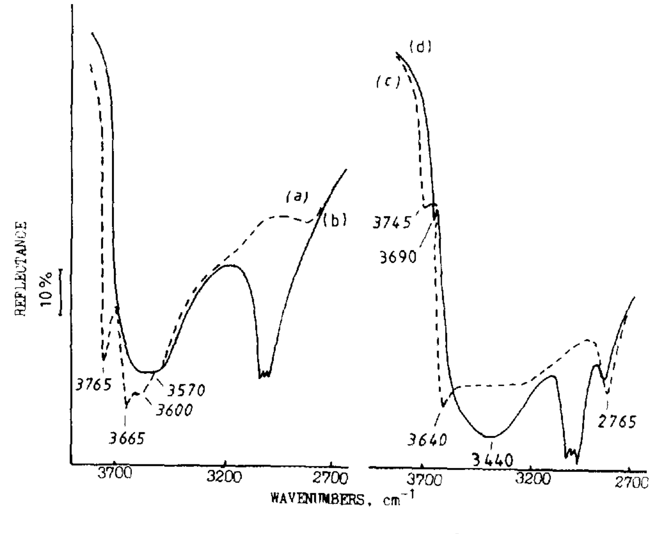


FIG. 4. IR spectra of ZrO$_2$ (a, b) and 5% SO$_4^{2-}$/ZrO$_2$ (c, d) (surface area = 290 m^2/g) measured before (a, c) and after (b, d) benzene adsorption at 300 K.

TABLE 1

Low-Frequency Shifts $\Delta \nu_{OH}$ for Various OH Groups after Benzene Adsorption

Type of OH group	ν_{0-1} (cm^{-1})	$\Delta\nu_{0-1}$ (C_6H_6) (cm^{-1})
SiOH in SiO_2	3750	120–140
ZrOH in ZrO_2	3670	100
ZrOH in SO_4^{2-}/ZrO_2	3640	200
Si(OH)Al in HX zeolite	3660	240–260
Si(OH)Al in HY zeolite	3640	280–320
Si(OH)Al in H-ZSM-5 zeolite	3610	350

tion of C_6H_6 (10 Torr, 300 K) on nonmodified and modified zirconia samples. For nonmodified ZrO_2 the frequency shift due to the formation of a hydrogen bond between C_6H_6 molecules and surface OH groups is rather small and an unresolved broad band of H-bonded complexes appears at 3570 cm^{-1} (Figs. 4a and 4b). For the modified sample the corresponding shift of about 200 cm^{-1} is considerably larger (Figs. 4c and 4d). Thus, modification with SO_4^{2-} anions results in enhancement of the acid strength of surface ZrOH groups.

However, even for the modified samples, the low frequency shift due to H bonding with benzene molecules is still much lower than that reported for H forms of zeolites which are known to exhibit strong (but not superacidic) Brønsted acidity. Indeed, for H-ZSM-5 zeolite the corresponding $\Delta\nu$ value is close to 350 cm^{-1}, while for HY zeolite it ranges from 280 to 320 and 240 to 260 cm^{-1} for HX zeolite (15) (Table 1). On the other hand, for silanol groups in SiO_2 the frequency shift of the band at 3750 cm^{-1} after benzene adsorption is about 120–140 cm^{-1}. Thus, the Brønsted acid sites in zirconium dioxide modified by SO_4^{2-} anions are stronger than the silanol groups of silica gel, but weaker than the bridging OH groups in HX zeolites. In other words, they cannot be classified as "superacid" ones.

Unfortunately, the similar "hydrogen bonding" approach cannot be used to estimate the strength of multicenter bonded protons responsible for the broad absorption band at 3250–2950 cm^{-1}. Therefore we used for this purpose the test reaction of olefin oligomerization at room temperature. The latter is known to proceed on strong Brønsted acid sites in zeolites (16–18) and in other acid type catalysts (19, 20). For instance, bridging OH groups in ZSM-5 zeolites are responsible for fast oligomerization of ethylene, propylene and cyclopropane at room temperature, resulting in predominant formation of linear oligomers which fill the channels of the zeolite framework.

Figure 5 presents the IR spectra of the unmodified ZrO_2 measured (a) 10 min and (b) 12 h after admission of C_2H_4 or cyclopropane (c) at 300 K. In both cases no fast oligomerization takes place and the intense bands attributed to adsorbed reactant molecules with ν_{as} = 3100 cm^{-1}, ν_s = 3005 cm^{-1} for C_2H_4 and ν_{as} = 3100 cm^{-1}, ν_s = 3015 cm^{-1} for cyclopropane are more intense in the spectra. The bands of C_2H_4 are slightly shifted as compared with the gas phase (ν_{as} = 3095 cm^{-1}, ν_s = 2995 cm^{-1} (21)) probably because of the interaction with Lewis acid sites via π-complex formation (see the next section). After 20-min exposure only weak absorption bands appear at 2980, 2930, and 2860 cm^{-1}, which may be ascribed to oligomerization products. Their intensities increase very slowly. Even after keeping the samples with preadsorbed C_2H_4 for 12 h they are considerably weaker as compared with the intensities of the bands attributed to unreacted olefin. In the case of cyclopropane transformation, the unmodified ZrO_2 is even less active than in oligomerization of C_2H_4.

Unlike the parent ZrO_2, the samples modified with SO_4^{2-} anions exhibited excellent activity in both C_2H_4 and cyclopropane oligomerization, comparable to that H-ZSM-5 zeolites. In Fig. 6 the changes of the IR spectra observed after C_2H_4 (a)–(c) or cyclo-C_3H_6 (e), (d) adsorption on sulfated zirconia are presented. Ethylene admission results in immediate (after a 10-min exposure) appearance of intense bands at 2970, 2930, and 2860 cm^{-1}, attributed to $\nu_{as}(CH_3)$, $\nu_{as}(CH)$, and $\nu_s(CH_2, CH_3)$ vibrations of oligomers. The bands of CH_2 fragments are more intense in the spectra, thereby indicating that preferentially linear oligomeric chains are formed in contradiction with a classical carbenium-ion mechanism.

Further increase of the "contact time" to 12 h leads to a further decrease of the bands of ethylene in the gas

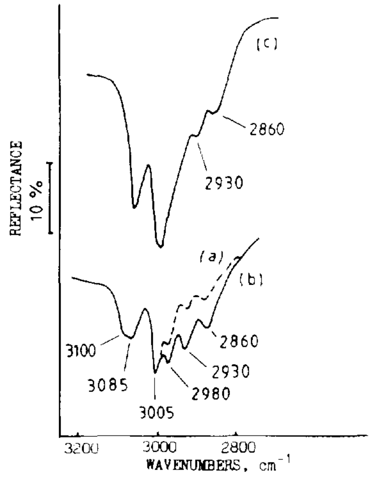


FIG. 5. IR spectra of ZrO_2 (surface area = 290 m^2/g) measured at 10 min (a) and 12 h (b, c) after adsorption of 10 Torr C_2H_4 (b) and cyclopropane (c).

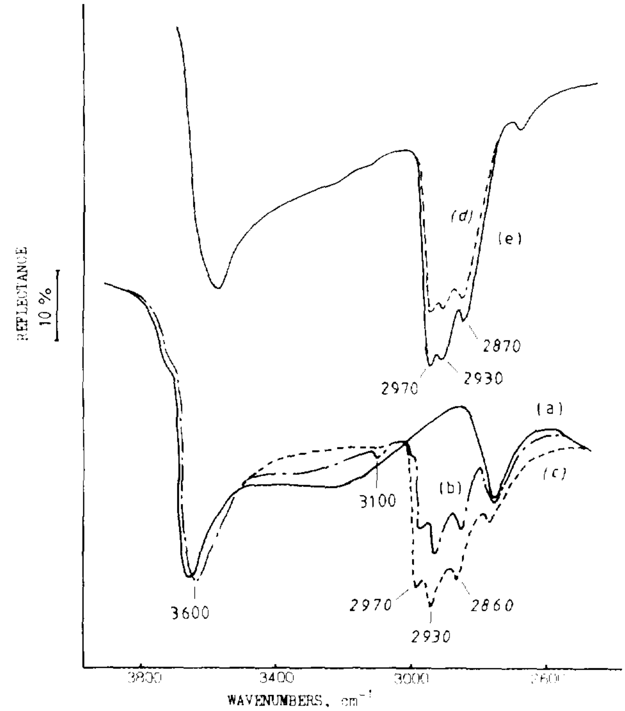


FIG. 6. IR spectra of 5% SO_4^{2-}/ZrO_2 (surface area = 290 m^2/g) measured before (a) and after 10 min (b, d) and 12 h adsorption of 10 Torr C_2H_4 (b, c) and cyclopropane (e, d) at 300 K.

phase (3100 and 2995 cm^{-1}), a drop of the pressure to zero and to the growth of the bands attributed to oligomerization products. The rate of formation of oligomers deduced from these spectra is faster than that reported on H-ZSM-5 zeolite which requires about 30–40 min (18a). The admission of an additional amount of ethylene to the sample, kept with preadsorbed C_2H_4 for 12 h, causes subsequent growth of the IR bands assigned to oligomerization products. The very important feature of these spectra concerns the broad band at 3250–2950 cm^{-1}, which substantially decreases after the admission of olefin. Such a behavior of this type of protons is indicative of their participation in the above reaction.

A similar evolution of the IR spectra was also observed after admission of cyclopropane onto the sulfated zirconia (Figs. 6d and 6e). However, unlike C_2H_4, fast transformations of cyclo-C_3H_6 result in branched oligomers containing rather high concentrations of CH_3 fragments characterized by the IR-bands at 2970 and 2870 cm^{-1}.

As shown previously (16, 17, 20) olefin oligomerization may take place both on strong Brønsted and on strong Lewis acid sites. To distinguish these two mechanisms we investigated oligomerization of deuteriated ethylene. If Brønsted acid sites are responsible for the reaction, fast H–D exchange between proton sites and olefin molecules should be expected, in accordance with our previous results. If Lewis acid sites are involved in oligomerization, no H–D exchange should take place during the reaction.

Figure 7 shows the IR spectra of a SO_4^{2-}/ZrO_2 sample after C_2D_4 adsorption at 300 K. It follows from these spectra that fast H–D exchange proceeds after admission of deuteriated olefin resulting in formation of CHD fragments (ν_{CH} = 2890 cm^{-1} and OD species (ν_{OD} = 2760–2490 cm^{-1}). Oligomerization results in slightly branched oligomers characterized by the corresponding absorption bands of CD_2 groups (ν_{as} = 2200 cm^{-1}, ν_s = 2095 cm^{-1}). OD species formed via H–D exchange are mainly surface deuteroxyls with the frequency of the stretching vibrations at 2690 cm^{-1} (OH analogue at 3650 cm^{-1}) and those hydrogen-bonded with oligomer chains (ν_{OD} = 2650 cm^{-1}, OH analogue at 3580 cm^{-1}).

Thus, modification of zirconia with sulfate anions was shown to result in the following changes:

(1) it enhances the strength of the bridged ZrOH groups and eliminates the terminal ZrOH species;

(2) it creates a new type of Brønsted acid sites, presumably protons forming multicenter bonds with sulfate anions.

(3) it also gives rise to a high activity in oligomerization of ethylene and cyclopropane at room temperature accompanied with H–D exchange between substrate molecules and Brønsted acid sites responsible for the reaction.

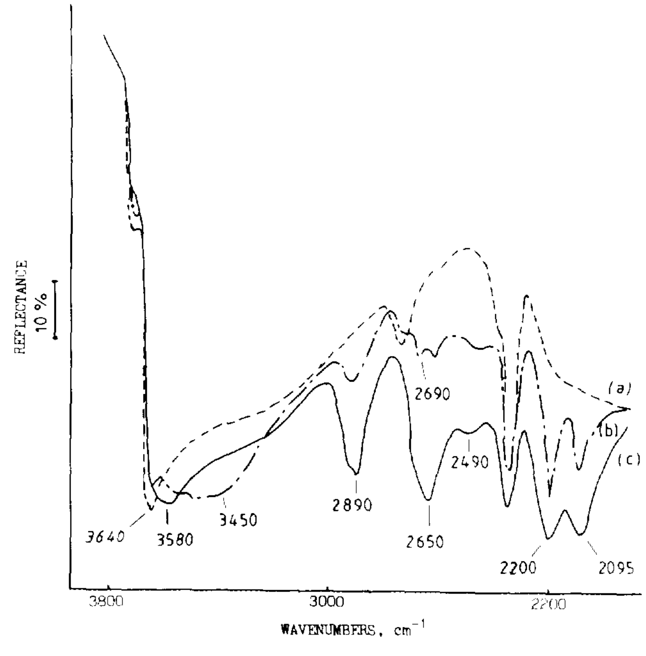


FIG. 7. IR spectra of 5% SO_4^{2-}/ZrO_2 (surface area = 290 m^2/g) measured before (a) and after 10 min (b) and 12 h (c) adsorption of 10 Torr C_2D_4 at 300 K.

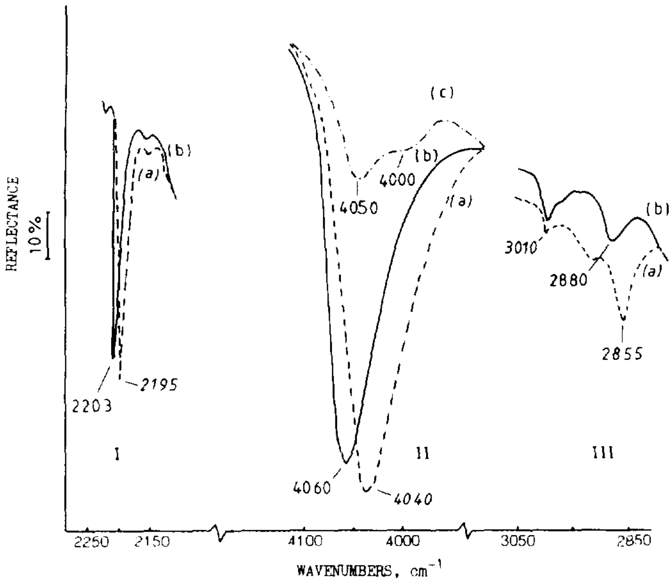


FIG. 8. IR spectra of ZrO_2 (surface area = 290 m^2/g) and (b) 5% SO_4^{2-}/ZrO_2 (surface area = 5 m^2/g) after adsorption of CO at 300 K (I), H_2 at 77 K (II), and 20 Torr CH_4 at 300 K (III).

2. *Lewis Acidity*

Lewis acid sites in sulfated zirconia were studied using the adsorption of different IR molecular probes: H_2 (12), CO (20), and CH_4 (21). CO is known to be a suitable probe for electron-accepting sites, whereas H_2 or CH_4 are found to test Lewis acid–base pairs consisting of low-coordinate metal ions (Lewis acid sites) and neighboring oxygen anions (Lewis basic sites) (23, 24).

Figures 8 Ia and Ib reports the IR spectra of CO adsorbed at 300 K on ZrO_2 and SO_4^{2-}/ZrO_2. For unmodified zirconia an intense band at 2185-2195 cm^{-1} corresponds to CO complexes with Lewis acid sites, its maximum being dependent on the origin and surface area of ZrO_2. The position of this band and the value of the high frequency shift as compared with the CO stretching frequency in the gas phase (2143 cm^{-1}) is evidence for a moderate strength of Lewis acid sites available at the surface of unmodified zirconia.

After sulfate treatment this band is shifted to higher frequencies (Fig. 8 Ib) thus indicating a small but distinct increase of the acid strength of Lewis acid sites probably via an inductive effect of SO_4^{2-} anions withdrawing electron density through the framework. The concentration of Lewis acid sites estimated by the relative intensity of the CO band does not change after modification.

The IR spectra of molecular hydrogen adsorbed at 77 K on the samples under study are presented in Fig. 8 IIa–IIc. As in the case of CO, both for the initial ZrO_2 and for the sulfated ZrO_2 a single absorption band is present in the spectra. For untreated ZrO_2 its maximum (4040 cm^{-1}) is red-shifted by 123 cm^{-1} as compared with the gas phase (ν_{H-H} = 4163 cm^{-1}), whereas for sulfated ZrO_2 the corresponding IR low-frequency shift is equal only to 103 cm^{-1}.

Taking into account that:

(i) according to the above data on CO adsorption the modification of ZrO_2 with SO_4^{2-} anions results in an increase of the acid strength of Lewis acid sites, and that

(ii) unlike CO, hydrogen is a probe for Lewis acid–base pairs,

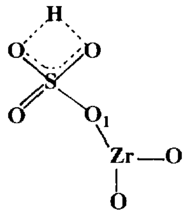
one may conclude that the smaller H–H low frequency shift for sulfated ZrO_2 seems to be an indication of a less basic character of oxygen anions in the acid–base pairs.

In the spectrum of sulfated zirconia with a low surface area (5 m^2/g) in addition to the band at 4050 cm^{-1} a low-intensity absorption band at 4000 cm^{-1} is also observed (Fig. 8 IIc).

The IR-spectra of CH_4 adsorbed at 300 K on the modified and unmodified ZrO_2 are shown in Figs. 8 IIIa and IIIb. The spectrum of untreated sample IIIa contains weak absorption bands at ν_{as} = 3010 cm^{-1} attributed to physically adsorbed methane and an intense band at 2855 cm^{-1}. In agreement with Ref. (23) the latter could be assigned to the shifted ν_{as} band of polarized CH_4 molecules adsorbed by Lewis acid sites.

The IR-spectrum of CH_4 adsorbed on sulfated ZrO_2 is similar to that observed for the unmodified sample except for the position of the absorption band ascribed to CH_4 molecules polarized by Lewis acid sites, which is found at 2880 cm^{-1} instead of 2855 cm^{-1}. Thus, as in the case of molecular hydrogen, the low frequency shift for methane complexes with Lewis acid–base pairs in sulfated ZrO_2 is smaller ($\Delta\nu$ = 138 cm^{-1}) as compared with untreated ZrO_2 ($\Delta\nu$ = cm^{-1}). This again indicates the weaker polarizing properties of acid–base pairs in the sulfated sample despite stronger Lewis acid sites in these pairs as evidenced by CO adsorption. Such a weakening of the polarizing ability of the acid–base pairs may be accounted for, as in the case of H_2, by a less basic character of oxygen anions in sulfated ZrO_2 due to an inductive effect of SO_4^{2-} anions or the presence of acidic protons in the vicinity of a Lewis acid site. Thus, modification of ZrO_2 with SO_4^{2-} anions results in a strengthening of the Lewis acid sites represented by low-coordinate zirconium ions and in a weakening of the polarizing ability of Lewis acid–base pairs.

To understand the mechanism of such modification of Lewis acid–base properties of zirconia by HSO_4^- anions the previous structure (III) may be used. The electron-accepting properties of three-coordinate zirconium cations are enhanced via the inductive effect of the SO_4^{2-} anion withdrawing electron density from zirconium or via its direct interaction with the O_1 atom of the sulfate group (Scheme 3).



(V)

SCHEME 3

CONCLUSION

The results of this study show that the acid properties of zirconium dioxide modified with sulfate anions are connected with the surface HSO_4^- groups formed by substitution of the terminal ZrOH groups of sulfate anions. The protons of such Brønsted sites are hydrogen-bonded with neighboring basic oxygens of sulfate ions or with basic oxygens of the zirconium dioxide support, resulting in very broad IR bands. In addition the modification enhances the strength of the parent Brønsted and Lewis sites of the zirconium dioxide carrier. However, this effect is much weaker and cannot explain the superacidic properties of modified samples.

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