Catalysis Letters 30 (1995) 31–39

IR characterization of sulfated zirconia derived from zirconium sulfate

E. Escalona Platero [1] and M. Peñarroya Mentruit

Departamento de Química, Universidad de las Islas Baleares,
07071 Palma de Mallorca, Spain

Received 8 August 1994; accepted 21 October 1994

Surface characterization of a sulfate-derived zirconia sample containing approximately 1 wt% S was performed by IR spectroscopy. Several types of sulfate groups were detected which are resistant to heating in vacuo up to 973 K. By using CO as a spectroscopic probe, two kinds of Lewis acid sites were identified which were assigned to surface Zr^{4+} ions in different environments. Comparison with corresponding data for a nearly sulfate-free zirconia sample showed that sulfated zirconia has an enhanced Lewis acidity.

Keywords: sulfated zirconia; infrared spectroscopy; CO adsorption

1. Introduction

Pure zirconia is a material with relevant applications as an acid catalyst and also as a catalyst support. As a catalyst, ZrO_2 is known to be active in chemical processes, such as, among others, methanol synthesis and alcohol dehydration [1,2]. However, acidity of pure zirconia is too weak for catalysing more demanding processes where strong acids are needed. Doping of ZrO_2 with sulfate groups is known to be a means to increase acidity. In fact, sulfated zirconia acts as an active catalyst [3–7] for skeletal isomerization of paraffins (even under mild conditions), which is a process demanding the agency of strong acid centres.

Sulfate-modified zirconia is usually prepared by impregnation (followed by calcination) of ZrO_2, or a zirconia gel, with sulfuric acid or an ammonium sulfate solution [3–10], or by treating zirconia with sulfur oxides in excess oxygen [11]. These procedures lead to formation of several types of sulfate and polysulfate groups on the zirconia surface, which are reported [7,12–14] to be responsible for increased acidity. The nature of the acid centres is not clearly established, and in particular it is a matter of debate [5,9,11,15,16] whether Lewis or Brønsted sites are involved in

---

[1] To whom correspondence should be addressed.

the catalytic properties of sulfated zirconia. On the other hand, the nature and strength of surface acid sites is known to be dependent upon many preparative parameters [14].

Sulfated zirconia can also be prepared by thermolysis of zirconium sulfate [17,18]. Following this procedure, sulfate groups from the precursor material are retained on the zirconia surface and no further sulfating treatment is required. However, no studies have been reported to date on the surface chemistry of these materials. This paper describes an IR investigation of the sulfate groups and Lewis acidity at the surface of a sulfated zirconia prepared by thermolysis of zirconium sulfate. CO was used as an IR spectroscopic probe.

2. Experimental

Sulfated zirconia (hereafter ZRS) was prepared by thermal decomposition, at 1000 K in air, of $Zr(SO_4)_2 \cdot 4H_2O$ (BDH, analytical grade). Structural and textural (surface area and porosity) characterization of this material was reported elsewhere [18]. The ZRS sample was found to be basically in the monoclinic form (a small proportion of tetragonal phase was also observed) and it showed a BET surface area of 90 $m^2 g^{-1}$ and a most frequent pore radius of 8 nm. Chemical analysis showed a residual sulfur content of 1.1%.

For IR studies, the ZRS sample in the form of a self-supporting disk (0.03 g cm^{-2}) was placed inside a vacuum cell which allowed in situ activation, dosing with CO and acquisition of IR spectra. For activation, the zirconia wafer was heated in a dynamic vacuum (residual pressure 10^{-3} Pa) for 30 min at increasing temperature, from 373 up to 1173 K. After each activation period, the sample was allowed to cool to room temperature and IR spectra were taken. Activated samples are hereafter termed ZRSx, where x indicates the temperature of the last heat treatment. Thus, ZRS473 is a ZRS sample heated in vacuo for 30 min at 373 K followed by 30 min at 473 K. Room temperature IR transmission spectra were recorded, at 3.2 cm^{-1} resolution, by using a Perkin–Elmer 881 spectrometer equipped with the corresponding personal computer.

3. Results and discussion

3.1. IR SPECTRA OF SULFATED ZIRCONIA: O–H STRETCHING REGION

Fig. 1 depicts IR spectra in the 4000–3300 cm^{-1} region for the different zirconia samples. ZRS (sample not activated) shows a very broad IR absorption starting at about 3750 cm^{-1} and extending down to 3300 cm^{-1}. This broad band can be assigned to H-bonded hydroxyl groups, coupled with physisorbed water molecules. This last contribution is confirmed by an intense IR absorption band centred at

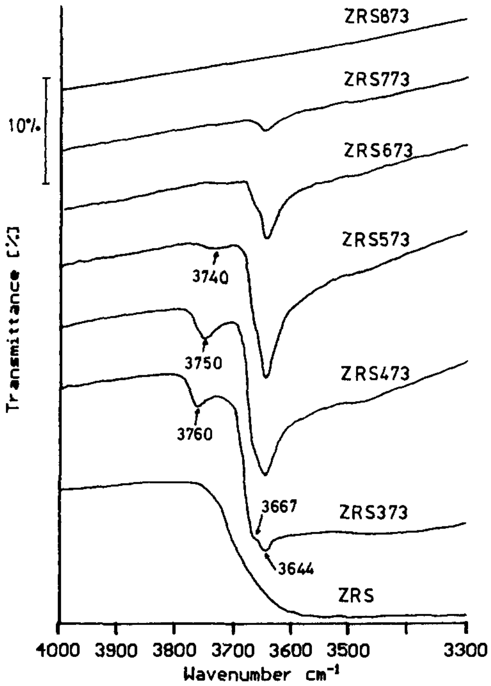


Fig. 1. IR spectra in the O–H stretching region of sulfated zirconia samples activated at increasing temperature.

1630 cm^{-1} (fig. 2), which corresponds to the H_2O bending mode. Activation at 373 K (sample ZRS373) results in partial elimination of adsorbed water and parallel appearance of distinct IR absorption bands at 3760, 3667(sh) and 3644 cm^{-1}. Further heating in vacuo at increasing temperature brings about gradual changes as follows (fig. 1): (i) progressive elimination of physisorbed water, (ii) decrease in intensity and shift towards lower frequency of the 3760 cm^{-1} band, which disappears in ZRS673, and (iii) diminishing intensity of the 3667–3644 cm^{-1} doublet which is no longer present in ZRS873.

The IR spectrum of pure zirconia (containing no sulfate groups) activated at 773 K was reported [11,19–21] to show O–H stretching bands at 3775 and 3668 cm^{-1}, which were assigned respectively to terminal hydroxyls and to bridged Zr(OH)Zr groups. These bands should correspond to those at 3760 cm^{-1} (terminal OH) and at 3667 cm^{-1} (bridged OH) of the ZRS373 sample (fig. 1). The IR absorption observed at 3644 cm^{-1}, which becomes the dominant feature of the spectra for samples activated at higher temperature (up to 773 K), has no equivalent in sulfate-free ZrO_2. However, for sulfated zirconia several workers have reported a similar IR absorption band. Thus, Komarov and Sinilo [9] found two O–H stretching bands, at 3635 and at 3655 cm^{-1}, for sulfated zirconia prepared by impregnation of a hydrous gel with H_2SO_4, and Bensitel et al. [11] found an analogous 3655 cm^{-1} band for sulfated zirconia obtained by heating ZrO_2 with SO_2

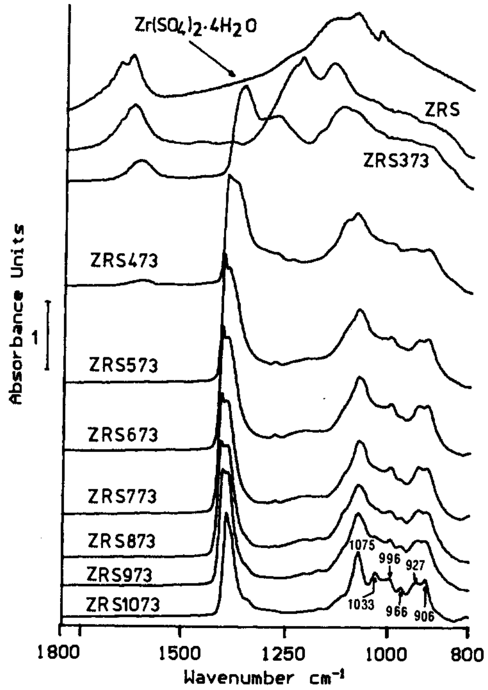
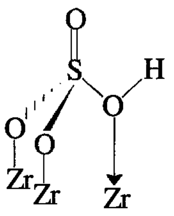


Fig. 2. IR spectra, in the sulfate region, of the parent zirconium sulfate and of sulfated zirconia activated at increasing temperature.

in an oxygen excess. It thus appears that this low frequency band, which in our samples appears at 3644 cm^{-1}, must be assigned to hydroxyls perturbed by neighbouring sulfate groups. The exact structure of these Brønsted acid centres is not known, and it could be dependent on the sample preparation procedure as suggested by the reported variations of O–H stretching frequency. Note, however, that from a recent study which combines Raman and ^{1}H MAS NMR spectroscopy Riemer et al. [22] have proposed for the surface SO_4 groups of sulfated zirconia the structure



A structure of this type would explain the observed lowering of O–H stretching frequency through an inductive effect from the neighbouring sulfate group.

3.2. S–O STRETCHING REGION

Fig. 2 shows IR spectra in the 1800–800 cm^{-1} region for the different zirconia samples. All of them are difference spectra obtained by subtracting the spectrum corresponding to a ZRS1173 sample (not shown) in which the S–O stretching band had a vanishing small intensity.

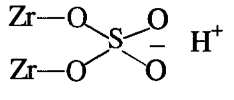
For comparison, the IR spectrum corresponding to the parent $Zr(SO_4)_2 \cdot 4H_2O$ material is also depicted in fig. 2. This spectrum shows a double band at about 1650 cm^{-1} corresponding to bending modes of H_2O, and a broad IR absorption at about 1100 cm^{-1}, in which three components can be discerned. These correspond to the ν_3 mode of sulfate groups which gives three bands (A_1, B_1, B_2) when the symmetry is lowered from T_2 to C_{2v}.

The spectra in fig. 2 show that molecular water (1640 cm^{-1} band) is progressively eliminated on increasing the activation temperature and completely disappears in the sample activated at 573 K. Two groups of sulfate bands are observed, at about 1400 cm^{-1} and in the 1100–800 cm^{-1} region, respectively.

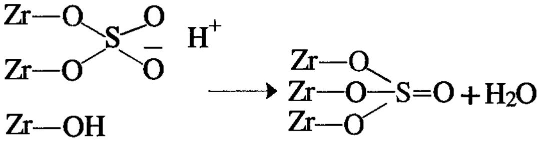
In agreement with reported data [8,14], the complex 1400 cm^{-1} band is assigned to the stretching mode of surface sulfate species containing a single S=O group. The asymmetric stretching of species containing the O=S=O moiety would also give IR absorption at about 1400 cm^{-1}, but in this case a second band should be observed at 1150–1200 cm^{-1} due to the corresponding symmetric stretching mode [23]. Absence of this band excludes sulfate species containing two double bonds on the same sulfur atom. The fact that the 1400 cm^{-1} band has several components is assigned, according to Bensitel et al. [8] and to Morterra et al. [14], to the simultaneous presence of different sulfate groups which could be isolated $(Zr{-}O)_3{-}S{=}O$ and polynuclear species, most likely disulfates: $[(Zr{-}O)_2(SO)]_2{-}O$. The latter would give components at $\nu > 1400$ cm^{-1}, while the S=O stretching mode of $(Zr{-}O)_3{-}S{=}O$ is expected at $\nu < 1400$ cm^{-1} [14].

The group of bands observed in the 1100–800 cm^{-1} region is assigned to the stretching modes of single S–O bonds [8,14]. The presence of six IR absorption bands in this frequency range confirms the existence of different sulfate species.

The observed variation of the IR spectra in fig. 2 can be explained as follows. When sulfated zirconia is fully hydrated (ZRS sample) the corresponding IR spectrum is similar to that of the parent material ($Zr(SO_4)_2 \cdot 4H_2O$) and can be assigned to ionic species of the type



in which only the low frequency bands (ca. 1100 cm^{-1}) are present, in agreement with the absence of covalent S=O bonds (1400 cm^{-1} band). Elimination of water molecules brings about increased covalency of the sulfur–oxygen bond, with consequent development of the 1400 cm^{-1} band. According to Waqif et al. [13] and to Lange et al. [24], dehydration proceeds as follows:



A similar process can be proposed for the formation of disulfate species,

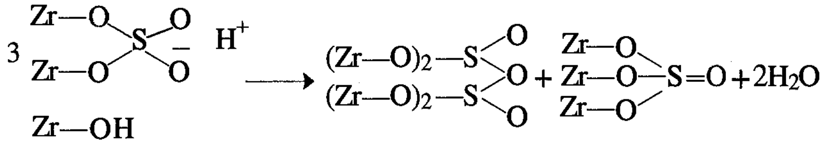


Fig. 2 also shows that for samples ZRS573 to ZRS973 the intensity of the sulfate bands (both at 1400 cm^{-1} and in the 1100–800 cm^{-1} region) is approximately constant. However, for ZRS1073 a significant decrease is observed. From these facts it can be concluded that sulfate groups are resistant to the thermal treatment in vacuo up to 973 K, and they are progressively eliminated at higher temperature. The remaining sulfur content in ZRS1073 was evaluated, semiquantitatively, as 0.70% (from the corresponding integrated intensity of the IR bands) assuming that the initial value of 1.1% (determined by chemical analysis) is preserved in ZRS573 since sulfates are not likely to be thermolysed at 573 K [6,7,14]. Note that for samples ZRS, ZRS373 and ZRS473 determination of the intensity of sulfate IR bands cannot be effected, due to the strong contribution from molecular water.

3.3. LEWIS ACIDITY

Fig. 3 shows the IR spectra in the C–O stretching region of carbon monoxide adsorbed (at room temperature) on samples ZRS1073 and ZRS1173. This last sample was found to give negligible IR absorption from sulfate groups and can thus be considered as a nearly sulfate-free zirconia.

CO adsorbed on ZRS1173 shows two partially overlapping IR absorption bands which for small CO dosis appear at 2201 and at 2188 cm^{-1}, respectively. They were also observed (at nearly the same frequencies) by Morterra et al. [25] for CO adsorbed on pure ZrO_2, and assigned to coordinatively unsaturated Zr^{4+} ions (Lewis acid sites) at the surface of the metal oxide. It is generally agreed [26,27] that interaction of the dipolar CO molecule, via the carbon atom, with coordinatively unsaturated cations at the surface of metal oxides and halides results in a hypsochromic shift of the C–O stretching frequency from the value of 2143 cm^{-1} corre-

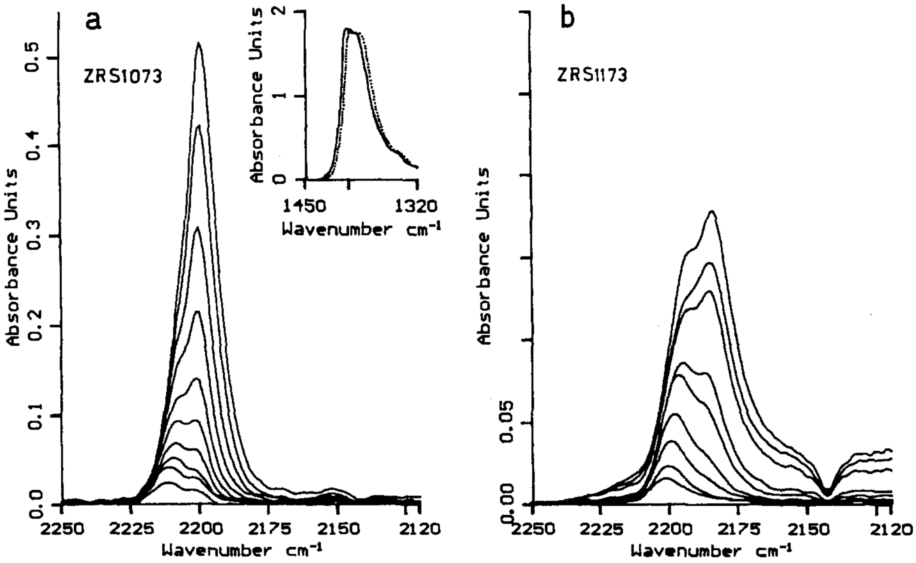


Fig. 3. IR spectra of increasing doses (10^{-2}– 30 Torr) of CO on (a) ZRS1073 and (b) ZRS1173 samples. The inset shows the S=O band prior to (—) and after (...) dosing 30 Torr of CO on the ZRS1073 sample.

sponding to the free carbon monoxide. This hypsochromic shift is a consequence of both polarization of the CO molecule (by the surface cation) and partial charge transfer [28,29]. The presence of two IR absorption bands for CO adsorbed on ZRS1173 (and also on pure ZrO_2) clearly indicates the existence of two different groups of Lewis acid sites. They should correspond to Zr^{4+} ions in different environments, presumably due to exposure of different (*hkl*) planes. Fig. 3b also shows that on increasing the CO equilibrium pressure (up to 30 Torr) both IR absorption bands slightly shift towards lower frequency values, which are summarized in table 1. This effect can be ascribed to the progressive build up of absorbate–adsor-

Table 1
Position of IR absorption maxima for CO adsorbed (at low coverage) on different zirconia samples

Sample	ν_{CO} (cm^{-1})	Ref.
sulfated zirconia from zirconium sulfate (samples ZRS773 to ZRS1073)	2212 (m) 2202 (vs)	this work
sulfate-doped zirconia	2212 (m) 2202 (vs)	[11]
non-sulfated zirconia (sample ZRS1173)	2201 (s) 2188 (s)	this work
pure zirconia	2199 (s) 2188 (s)	[25]

bate interactions [26,30]. Table 1 summarizes the observed IR absorption maxima for the different zirconia samples. For comparison, corresponding literature values are also reported.

Fig. 3a shows the spectra of CO adsorbed (at increasing equilibrium pressure) on ZRS1073 (samples ZRS773, ZRS873 and ZRS973 gave entirely similar spectra, table 1). Two partially overlapping bands are also observed, but they are shifted to higher frequency, when compared with ZRS1173. This shows that presence of sulfate groups considerably increases Lewis acidity of surface Zr^{4+} ions, presumably due to an inductive effect [7,12]. A similar result was found by Bensitel et al. [11], who investigated zirconia previously treated with sulfur oxides. We note that the higher frequency band in fig. 3a saturates more rapidly than the low frequency component, which also testifies to a correspondingly higher Lewis acidity of the involved surface sites.

Finally, the inset in fig. 3a shows that on CO adsorption the sulfate band at ca. 1400 cm^{-1} slightly shifts to lower frequency. Small variations were also found in the 1100–800 cm^{-1} bands. These effects strongly suggest that sulfate groups are mainly exposed at the zirconia surface.

In conclusion, we have investigated an alternative method for the preparation of sulfated zirconia, which uses zirconium sulfate as a precursor and avoids the need for chemically doping with a sulfating agent. The product obtained showed an acidity comparable to that one reported in the literature for sulfate-doped ZrO_2. A further advantage of using zirconium sulfate as a precursor can be the observed thermal stability of the oxide product obtained.

Acknowledgement

This research was supported by the Spanish DGICYT, project PS90-0214. The authors thank Professor C. Otero Areán for helpful discussions.

References

[1] N.B. Jackson and J.G. Ekerdt, J. Catal. 101 (1986) 90.

[2] K. Maruya, T. Maehashi, T. Haraoka, S. Narui, K. Domen and T. Onishi, J. Chem. Soc. Chem. Commun. (1985) 1494.

[3] K. Arata, Adv. Catal. 37 (1990) 165.

[4] J.M. Parera, Catal. Today 15 (1992) 481.

[5] P. Nascimento, C. Akratopoulou, M. Oszagyan, G. Coudurier, C. Travers, J.F. Joly and J.C. Vedrine, *Proc. 10th Int. Congr. on Catalysis*, Budapest 1992 (Elsevier, Amsterdam, 1993) p. 1185.

[6] F.R. Chen, G. Coudurier, J.F. Joly and J.C. Vedrine, J. Catal. 143 (1993) 616.

[7] E. Iglesia, S.L. Soled and G.M. Kramer, J. Catal. 144 (1993) 238.

[8] M. Bensitel, O. Saur, J.C. Lavalley and B.A. Morrow, Mater. Chem. Phys. 19 (1988) 147.

[9] V.S. Komarov and M.F. Sinilo, Kinet. Katal. 29 (1988) 605.
[10] C. Morterra, G. Cerrato, C. Emanuel and V. Bolis, J. Catal. 142 (1993) 349.
[11] M. Bensitel, O. Saur, J.C. Lavalley and G. Mabilon, Mater. Chem. Phys. 17 (1987) 249.
[12] K. Tanabe, Mater. Chem. Phys. 13 (1985) 347.
[13] M. Waqif, J. Bachelier, O. Saur and J.-C. Lavalley, J. Mol. Catal. 72 (1992) 127.
[14] C. Morterra, G. Cerrato and V. Bolis, Catal. Today 17 (1993) 505.
[15] T. Jin, T. Yamaguchi and K. Tanabe, J. Phys. Chem. 90 (1986) 4794.
[16] F. Babou, B. Bigot and P. Sautet, J. Phys. Chem. 97 (1993) 11501.
[17] K. Arata, M. Hino and N. Yamagata, Bull. Chem. Soc. Jpn. 63 (1990) 244.
[18] E. Escalona Platero and M. Peñarroya Mentruit, Mater. Lett. 14 (1992) 318.
[19] P.A. Agron, E.L. Fuller Jr. and H.F. Holmes, J. Colloid Interf. Sci. 52 (1975) 553.
[20] T. Yamaguchi, Y. Nakano and K. Tanabe, Bull. Chem. Soc. Jpn. 51 (1978) 2482.
[21] C. Morterra, R. Aschieri and M. Volante, Mater. Chem. Phys. 20 (1988) 539.
[22] T. Riemer, D. Spielbauer, M. Hunger, G.A.H. Mekhemer and H. Knözinger, J. Chem. Soc. Chem. Commun. (1994) 1181.
[23] L.G. Anello and R.F. Sweeney, J. Org. Chem. 35 (1970) 118.
[24] L. Lange, K. Hadjiivanov, H. Schmelz and H. Knözinger, Catal. Lett. 16 (1992) 97.
[25] C. Morterra and L. Marchese, *Proc. Int. Symp. on Acid–Base Catalysis*, Sapporo 1988 (Kodansha, Tokyo, 1989) p. 197.
[26] E. Escalona Platero, D. Scarano, G. Spoto and A. Zecchina, Faraday Discussions Chem. Soc. 80 (1985) 183.
[27] M.I. Saki and H. Knözinger, J. Catal. 119 (1989) 311.
[28] G. Pacchioni, G. Cogliandro and P.S. Bagus, Surf. Sci. 255 (1991) 344.
[29] K.M. Neyman and N. Rösch, Surf. Sci. 297 (1993) 223.
[30] R.F. Willis, A.A. Lucas and G.D. Mahan, in: *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, Vol. 2, eds. D.A. King and D.P. Woodruff (Elsevier, Amsterdam, 1982) ch.2.