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On determination of acid site densities on sulfated oxides

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Combined infrared and gravimetric studies have been performed of pyridine adsorption on sulfated and non-sulfated silica–zirconia mixed oxides in order to quantify the site densities of both Brønsted and Lewis acid sites. The values determined for the integrated molar absorption coefficients for the non-sulfated silica–zirconia mixed oxides were 1.24 cm μmol^{-1} at 1540 cm^{-1} and 1.56 cm μmol^{-1} at 1450 cm^{-1} and were independent of the Si : Zr ratio and other pre-treatment and preparation variables. On the other hand, values ranging from 0.64 to 1.66 cm μmol^{-1} at 1540 cm^{-1} for the pyridinium ion and from 1.00 to 2.08 cm μmol^{-1} for the Lewis-bound pyridine were determined for the sulfated samples. It is proposed that the reduction in absorption coefficient for the pyridinium ion with increasing sulfate density corresponds with the transformation of monomeric to dimeric or polymeric sulfate species which bring two adjacent adsorbed pyridine molecules into close proximity. The findings of this study raise considerable concern over the validity of acid site densities determined for sulfated materials where calculations have been performed based on literature values for the absorption coefficients.

KEY WORDS: surface acidity; sulfated oxides; pyridine; absorption coefficients.

1. Introduction

Acid catalysts are widely used in a number of industrially important reactions including isomerizations, alkylations, catalytic reforming of alkanes, cracking, and those involving oxygenated hydrocarbons. Solid acid catalysts are also being introduced into highly selective chemical and fine-chemical synthesis. The nature of the active site in solid acid catalysts is defined by the presence of protons, generating Brønsted acidity, and by coordinately unsaturated cationic centers giving Lewis acid sites [1]. The use of base molecule adsorption/desorption is well known for characterizing these systems and, in particular, the combination of vibrational spectroscopic techniques with pyridine or ammonia adsorption is routinely used following the pioneering works by Parry [2] and Peri [3]. The narrow-band widths of pyridine make this a particular favorite for infrared spectroscopic studies, giving good resolution of the 19b ring vibrational modes to distinguish between Brønsted (*ca.* 1540 cm^{-1}) and Lewis (*ca.* 1450 cm^{-1}) adsorbed forms. While many laboratories are content to quote the ratio of intensities of the two bands as a general indicator of the relative Lewis/Brønsted ratio, the combination of infrared spectroscopic with either volumetric or gravimetric adsorption studies makes the former an even more powerful tool by allowing the density of each type of adsorption site to be quantified *via* calculation of the absorption coefficients for each type of adsorbed species. Despite the apparent appeal of this combined approach, very few laboratories [4–7] have calculated values for coefficients, most preferring [8–11] to use the published values provided by Emeis [4] and Datka *et al.* [6] when calculating acid site densities. The reasoning behind this is the assumption that the two analytical bands above are expected to present molar extinction coefficients of virtually constant value in different oxidic systems [12].

Since the first publication appeared outlining the properties of sulfated zirconia as a catalyst [13], a vast volume of work has been published concerning the preparation, characterization and testing of these materials [10,13–16]. In terms of characterizing the acidic properties of these materials, some concern has already been expressed regarding the suitability of pyridine as a probe molecule [10,12]. These concerns are mainly focused on the competitive adsorption of sulfate and pyridine at the same Lewis sites which, if evaluated quantitatively, would overestimate the number of Lewis sites because of the use of such a hard (strong) base. It is assumed that if the adopted extinction coefficient is correct, then the estimated value of Brønsted site density is probably correct [10].

In the current paper we demonstrate that for a particular system (silica–zirconia), the extinction coefficients remain constant despite changes in preparation methods and zirconia concentrations and the significant changes in acid densities which ensue. However, the incorporation of sulfate into these systems leads to wide variation in the absorption coefficients, which, if not calculated for each particular sample, give rise to

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considerable errors in determining the total number of sites of each type.

2. Experimental

2.1. Sample preparation

A series of samples were prepared in which the zirconia content was varied from 9 to 75 mol%. Tetraethylorthosilicate (TEOS) was combined with water, propanol and 70 wt% nitric acid and stirred during 10 min pre-hydrolysis time. A 1:1 molar ratio of water to TEOS was used throughout. Zirconium tetrapropoxide was then added with simultaneous addition of water, propanol and 70 wt% nitric acid to give overall molar ratios of 1 [M^{4+}]:4 H_2O:4 propanol and 1 mole [Si^{4+}]:15 cm^3 70 wt% HNO_3 and 1 mole [Zr^{4+}]:50 cm^3 70 wt% HNO_3. All gels were redispersed in boiling ethyl acetate and refluxed for 4 h, before transferring to a critical point drying apparatus. The chamber was filled with liquid CO_2 at 298 K before raising the temperature to 320 K, to give a pressure of 8.685 MPa. The sample then remained in contact with the CO_2 for 4–6 h before changing the CO_2 while maintaining supercritical conditions. This process was repeated twice daily for 5 days. Calcination was performed at 773 K (2 h) in flowing air.

A number of sulfated 33 mol% zirconia–silica mixed oxide were prepared by modifying the method described by Yoldas [17]. TEOS (Silibond 90 wt%) was combined with water, propanol as a solvent, and nitric acid used as a hydrolysis catalyst. The above were combined in overall ratios of 1:1.2:1.5:0.2. The reagents were stirred under nitrogen for 2 h pre-hydrolysis time, after which zirconium isopropoxide (70 wt%) diluted 10:1 in propanol was added such that the ratio of $Si^{4+}:Zr^{4+}$ was 2:1. After a further hour the final amount of hydrolysis water was added dropwise, the final water:metal cation ratio being 2.6:1. All samples gelled within approximately 3 days. Propanol was then exchanged for ethyl acetate *via* Soxhlet extraction for 5 h, and the ethyl acetate was then subsequently removed using supercritical drying. Initially the sample was left for 12 h in supercritical CO_2 followed by a 30 min period of flushing every 2 h until no further ethyl acetate was detected in the effluent (typically after five flushes). Samples were then transferred to a tube furnace and calcined in flowing air at 873 K for 6 h. *In situ* sulfated samples were prepared in a similar manner but using sulfuric acid in varying amounts as the hydrolysis catalyst, the H^+ concentration being held constant by use of nitric acid. *Ex-situ* sulfation involved addition of appropriate amounts of 0.01 M sulfuric acid to a pre-calcined aerogel followed by further calcination at 873 K.

A series of samples, all containing 9 mol% Zr, were also prepared. 0.125 mol of tetramethyloxysilane and 10 cm^3 of 0.005 M HCl were added simultaneously to a vessel containing 1.098 mol of propan-1-ol. After vigorous stirring for 10 min, 0.01225 mol of zirconium 1-propoxide (70% soln) was added with stirring. A base-catalyzed sample was prepared in which the HCl was replaced by 10 cm^3 of 0.018 M NH_3. Both samples were supercritically dried in CO_2 as described above. Samples prepared by impregnation and precipitation routes involved the use of Aerosil 200. For the latter, the silica was suspended in water containing zirconium nitrate (MEL, 40% soln) and the zirconia was precipitated as the hydroxide by dropwise addition of 0.365 M ammonia solution. The precipitate was then filtered and washed. For the impregnation route, zirconium nitrate was again added to water containing the Aerosil 200 while continually stirring. Both samples were dried at 363 K for 16 h then calcined for 2 h at 773 K.

2.2. Experimental procedure

Surface acid densities were estimated using pyridine adsorption monitored by combined infrared spectroscopic and thermogravimetric techniques. The infrared experiments were carried out using *ca.* 80 mg of sample pressed (at 0.10 tons cm^{-2}) into 25 mm diameter discs. Spectra were recorded after the initial evacuation of the sample at 573 K and then after following exposure to pyridine and evacuation at 423 and 473 or 488 K. Thermogravimetric analyses were carried out using a PC-controlled CI microbalance attached to a conventional vacuum line fitted with rotary and oil diffusion pumps. Approximately 100 mg of sample as a fragmented pressed disc (prepared as per IR experiments) was evacuated for 2 h at 573 K, then exposed to 1 Torr pyridine and cooled to 373 K. A further 0.5 Torr of pyridine was introduced and the system allowed to reach equilibrium over 30 min. After this period, the sample was heated under vacuum to 423 K for 2 h, then at 473 (or 488) K for 2 h while monitoring the mass continually at 3 s intervals. The mass due to retained pyridine following evacuation at the two temperatures, in combination with the integrated areas underneath the bands at *ca.* 1450 and 1540 cm^{-1} due to the 19b ring vibrations of pyridine adsorbed at Lewis and Brønsted sites, respectively, at the corresponding temperatures allowed calculation of the respective absorption coefficients. The number of sites of each type was calculated by fitting the data to the equation

$$n_T = \frac{A_L C_d}{\varepsilon_L m} + \frac{A_B C_d}{\varepsilon_B m}$$

where n_T represents the total number of micromoles of pyridine per gram sample adsorbed at each temperature, A is the integrated absorbance (cm^{-1}) of IR bands due to pyridine adsorbed at Lewis (L) or Brønsted (B) sites, C_d is the cross-sectional area (cm^2) of the pressed disc, m is the mass (g) of the pressed disc, and ε is the molar absorption coefficient (cm μmol^{-1}) for pyridine at Lewis (L) or Brønsted (B) sites. As the equation contains two unknowns (the two molar absorption coefficients), at least two sets of data are required to solve the simultaneous equations and this is achieved by the measurement of n_T and A for at least two different outgassing temperatures. Combined IR–gravimetric experiments were repeated between three and five times to ensure that the values obtained for each sample were reproducible. The range of the calculated molar absorption coefficients was within ±5.5% of the values quoted in the tables.

3. Results

IR spectra of adsorbed pyridine on samples of varying mol% Zr revealed bands characteristic of both Lewis (1450 cm^{-1}) and Brønsted (1540 cm^{-1}) forms of adsorption. By combining IR and gravimetric measurements, absorption coefficients were calculated at each frequency for both forms of adsorbed species (table 1). These covered a relatively narrow range of values (1.16 to 1.32 at 1540 cm^{-1} for the pyridinium ion and 1.49 to 1.59 at 1450 cm^{-1} for the Lewis bound pyridine) with the average of 1.24 (at 1540 cm^{-1}) and 1.56 (at 1450 cm^{-1}) comparing well with values of 1.23 and 1.57 cm μmol^{-1} for 9 mol% silica–zirconia samples prepared by different methods [7], although somewhat lower than values of 1.67 and 2.22 cm μmol^{-1} quoted by Emeis [4]. The absorption coefficients allowed calculation of the surface densities of both types of acid site as detected by pyridine (table 1). A tenfold variation in Lewis site density and a fivefold variation in Brønsted site density was apparent across the range of samples.

Table 2 collects absorption coefficients and site densities for samples all containing 9 mol% Zr. Despite the considerable differences in the degrees of mixing expected by using sol–gel routes as opposed to precipitation or impregnation routes to incorporate the zirconia, the range of absorption coefficients is relatively small (1.21 to 1.27 at 1540 cm^{-1} for the pyridinium ion and 1.53 to 1.59 for the Lewis bound pyridine) The average of 1.23 (at 1540 cm^{-1}) and 1.56 (at 1450 cm^{-1}) compares very well with the average values of 1.24 and 1.56 cm μmol^{-1} for samples of varying mol% silica zirconias shown in table 1.

Table 1
Absorption coefficients and acid site densities for Si–Zr aerogels of varying Zr concentration.

Sample mol% Zr	ε_{1540}[a]	ε_{1450}[a]	$n_{\text{Brønsted}}$[b] (nm^2)	n_{Lewis}[b] (nm^2)
9	1.32	1.49	0.069	0.066
20	1.16	1.58	0.328	0.206
33	1.25	1.58	0.137	0.305
50	1.30	1.56	0.125	0.339
75	1.18	1.59	0.133	0.696

[a] IR absorption coefficient (cm μmol^{-1}).
[b] No. of acid sites per nm^2 (*i.e.*, no. of base molecules retained per nm^2 after evacuation at 423 K).

Table 2
Absorption coefficients and acid site densities for Si–Zr oxides containing 9 mol% Zr prepared by different methods.

Sample 9 mol% Zr	ε_{1540}[a]	ε_{1450}[a]	$n_{\text{Brönsted}}$[b] (nm^2)	n_{Lewis}[b] (nm^2)
Impregnation	1.26	1.55	0.072	0.215
Precipitation	1.21	1.58	0.163	0.447
HCl	1.27	1.59	0.11	0.20
NH_3	1.21	1.53	0.12	0.22

[a] IR absorption coefficient (cm μmol^{-1}).
[b] No. of acid sites per nm^2 (*i.e.*, no. of base molecules retained per nm^2 after evacuation at 423 K).

Table 3
Absorption coefficients and acid site densities for Si–Zr oxides all containing 33 mol% Zr, but of varying sulfate : Zr ratios produced by *in situ* and *ex situ* sulfation.

Sample	ε_{1540}[a]	ε_{1450}[a]	$n_{\text{Brönsted}}$[b] (nm^2)	n_{Lewis}[b] (nm^2)
SiZr (0.2 *in-situ*)	0.77	2.08	0.279	0.202
SiZr (0.25 *in-situ*)	0.66	1.74	0.253	0.204
SiZr (0.3 *in-situ*)	0.64	1.98	0.274	0.191
SiZr (0.2 *ex-situ*)	1.66	1.00	0.088	0.395
SiZr (0.25 *ex-situ*)	1.18	1.11	0.121	0.374
SiZr (0.3 *ex-situ*)	0.70	1.57	0.239	0.191

[a] IR absorption coefficient (cm μmol^{-1}).
[b] No. of acid sites per nm^2 (*i.e.*, no. of base molecules retained per nm^2 after evacuation at 423 K).

The absorption coefficients and site densities for sulfated silica–zirconia samples are collated in table 3. Note that the range of values obtained for the absorption coefficients is now much greater, with values ranging from 0.64 to 1.66 at 1540 cm^{-1} for the pyridinium ion and 1.00 to 2.08 for the Lewis bound pyridine. Although these values are wide-ranging for the different sulfated samples, the ranges still encompass the average values of 1.24 (1.23) (at 1540 cm^{-1}) and 1.56 cm μmol^{-1} (at 1450 cm^{-1}) for samples of varying mol% silica zirconias (table 1) or fixed mol% Zr (table 2).

4. Discussion

Experiments performed with a large number of non-sulfated silica–zirconia samples with results presented here and elsewhere [18] show that the molar absorption coefficients for adsorbed pyridine remain virtually constant irrespective of changes in preparation method or composition. The average values of 1.24 (at 1540 cm^{-1}) and 1.56 cm μmol^{-1} (at 1450 cm^{-1}) for all samples show very little deviation, although changes in sample preparation result in a range of surface site densities which varies tenfold for Lewis sites and fivefold for Brønsted sites. The values obtained here are somewhat lower than those obtained (1.67 at $1540\,\mathrm{cm}^{-1}$ and $2.22\,\mathrm{cm}\,\mu\mathrm{mol}^{-1}$ at $1450\,\mathrm{cm}^{-1}$) by Emeis [4] and which are the most widely quoted values in the literature. However, the values of Emeis [4] appear to be on the upper side of the range of published calculated values [5], with the lower side of the range being 0.73 at $1540\,\mathrm{cm}^{-1}$ and $1.11\,\mathrm{cm}\,\mu\mathrm{mol}^{-1}$ at $1450\,\mathrm{cm}^{-1}$ [6]. Our values reported here lie central to the range of literature values found. This fact, and the reproducibility of our results both in terms of the number of repeated experiments and the large number of samples prepared and tested in this study [18], gives us confidence in the determined values.

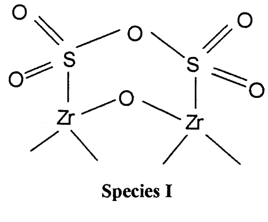
The values for the sulfated samples do, however, show a wide range of values for the calculated integrated molar absorption coefficients, ranging from 0.77 to $1.66\,\mathrm{cm}\,\mu\mathrm{mol}^{-1}$ at $1540\,\mathrm{cm}^{-1}$ and 1.00 to $2.08\,\mathrm{cm}\,\mu\mathrm{mol}^{-1}$ at $1450\,\mathrm{cm}^{-1}$ (table 3). These values still, however, fall within the range [5] of the extremes of values quoted in the general literature (0.73 to $1.67\,\mathrm{cm}\,\mu\mathrm{mol}^{-1}$ at $1540\,\mathrm{cm}^{-1}$ and 1.11 to $2.22\,\mathrm{cm}\,\mu\mathrm{mol}^{-1}$ at $1450\,\mathrm{cm}^{-1}$ [4,6]). Of concern is that by changing the density of surface sulfate groups, but keeping all other parameters (*e.g.*, Si : Zr ratio, pre-treatment temperature, outgassing temperature) which may affect acid site densities for sulfated zirconias [19], the coefficients can vary by a factor of two. This raises considerable concern over the validity of acid site densities determined for sulfated materials where the authors have performed calculations based on single-literature values. For example, plots of changes in site densities as a function of activation temperature [9,10] take on a very different appearance if the value for the absorption coefficient for either the pyridinium ion or the Lewis adsorbed pyridine is reduced to one-half of its value.

The reason behind these changing values for the absorption coefficients for sulfated materials, in contrast to their relative invariance for non-sulfated oxides and mixed oxides, merits attention. We have recently shown [20,21] for the *ex-situ* prepared sulfated silica zirconia samples, that strong Brønsted sites are generated once the sulfate surface density reached *ca.* $2.82\ \mathrm{SO_4/nm^2}$ (exposed zirconia), which corresponds with a density lying between that of samples SiZr (0.25 ex) and SiZr (0.3 ex). This value is significantly greater than the $1.52\ \mathrm{SO_4/nm^2}$ required to produce "superacid" properties on zirconia alone [22]. However, sites of similar strength on the *in-situ* sulfated materials appear even when the nominal S : Zr loading was 0.2. *i.e*, all *in-situ* sulfated samples in table 3 were able to catalyze double bond isomerization of but-1-ene. Although the equivalent non-sulfated silica zirconia had a similar density of Brønsted acid sites as the *in-situ* sulfated samples [20], it showed very low activity for but-1-ene isomerization [21] and was largely inactive for the alkylation of toluene by styrene [23]. There would appear, therefore, to be a parallel between the development of strong Brønsted acid sites and the detection of a low (*ca.* $0.7\,\mathrm{cm}^{-1}$ μmol) molar absorption coefficient (table 3) for adsorbed pyridinium ion. There is a degree of agreement that isolated surface sulfate species (present at low surface coverage) do not generate strong acid sites. However, at higher coverages, dimeric or polymeric species are generated which are responsible for the strong Brønsted acid sites [24]. It would appear that a relationship may exist between the appearance of such species and the drop in molar absorption for the adsorbed pyridinium ion.

Two possible reasons for the low absorption coefficient should be considered. Either (a) the adsorbed base molecule is electronically modified by adsorption on strong acid sites, or (b) the nature of the strong sites brings the adsorbates into sufficiently close proximity to each other that they experience intermolecular interactions not present in the non-sulfated oxides or at low sulfate coverages where isolated species predominate.

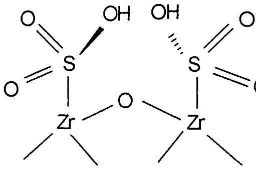
Emeis [4] made a strong case against the first of these possibilities by considering the fraction of sites which retained pyridine at the highest desorption temperatures and comparing values obtained with those obtained for molecules present at lower desorption temperatures. No variation in the absorption coefficient was found, although the material studied was a zeolite where one might expect the acid sites to be fairly homogeneous throughout the system.

This brings us to the possibility that the change in absorption coefficient occurs when the surface sulfate species are formed, which brings the adsorbed molecules into such close proximity that intermolecular forces result between adjacent adsorbates. The surface density of adsorbed pyridine for the non-sulfated mixed oxide always lies below $1.0/\mathrm{nm}^2$ (tables 1 and 2) [7,14,20]. Even allowing for non-homogeneous distribution over the surface, random distribution of sites at such low densities is unlikely to bring nearest-neighbor adsorbate molecules into such close proximity that intermolecular interactions are possible, and this is confirmed in the coverage-independent nature of the integrated molar absorption coefficient for pyridine adsorbed onto oxide surfaces [4,5,25]. IR analysis of the νS=O vibrations over the coverage range where isolated sulfate species are converted to polynuclear surface sulfates [19,22] suggests that the latter may take the form of a pyrosulfate, $(\mathrm{S_2O_7})^{2-}$, where each sulfur bridges two surface oxygen anions and the two sulfurs are bridged *via* a single bond to an oxygen (species I).



Species I

Ab-initio calculations predict that species I should give an intense maximum at 1400 cm^{-1} due to the νS=O [26]. Assuming that the Brønsted acidic protons are present as a hydroxyl located on the sulfate [9,27] rather than on the zirconia [15], the most likely manner [26] of generating Brønsted acid sites at the adsorbed pyrosulfate species following hydration of the samples would involve hydrolysis of the single bond S–O–S bridge to yield two close proximity hydroxyls, which would maintain the oxidation state and coordination number on the sulfur (species II).



Species II

Spectra in the OH stretching region contained a broad band centered at 3580 cm^{-1} and a sharper, better defined absorption at 3742 cm^{-1} due to silanols of the silica–zirconia support [7,25]. In the presence of sulfate, and independent of the degree of hydration, no additional features could be identified which would provide evidence for the presence of hydrogen-bonded hydroxyls on adjacent sulfate groups. Such hydroxyls have been observed, however, on phosphated silica–zirconia samples [21]. The generation of species II by hydration of species I would place two adjacent protonic sites at sufficiently close proximity that adsorbed, protonated base molecules would electronically interact, resulting in the lowering of the integrated molar absorption coefficient at 1540 cm^{-1} for the pyridinium ion which is seen in table 3. Changes in absorption coefficient as a function of adsorbate coverage have been used to identify the transition from a one-layer to a two-layer complex [28].

Note that while the integrated molar absorption coefficient at 1540 cm^{-1} for the pyridinium ion is reduced under conditions where strong acid sites have been generated (table 3), the value for the band due to the same vibrational mode (19b) for pyridine at Lewis acid centers is actually higher (1.5 to 2.0 cm μmol^{-1}, and closer to values for the non-sulfated materials) for samples where we believe the polynuclear sulfate species to be present. This leads us to tentatively suggest that it is in the presence of the mononuclear, isolated sulfate species that the Lewis sites (exposed zirconium ions) are electronically modified by their proximity to adsorbed sulfate. These Lewis acid sites are then lost as sulfate coverage is increased, and in the range of loadings where we have shown that each additional sulfate leads to the formation of 1 Brønsted acid site at the expense of *ca.* 1.5 Lewis sites [20]. Experiments are being performed to determine whether there is a change in Lewis acid site strength over the range of coverage where the transition from isolated to polynuclear sulfate species occurs.

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