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 Bronsted 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 Bronsted (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/Bronsted 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 acidic 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 tetr-propoxide was then added with simultaneous addition of water, propanol and 70 wt% nitric acid to give overall molar ratios of $[\text{M}^{4+}]:4\text{H_2O}:4$ propanol and 1 mole $[\text{Si}^{4+}]:15\text{cm}^3$ 70 wt% HNO$_3$ and 1 mole $[\text{Zr}^{4+}]:50\text{cm}^3$ 70 wt% HNO$_3$. All gels were dispersed 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 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 tetramethylxysilane 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 Bronsted (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 $\varepsilon$ is the molar