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On the environment of the active sites in phosphate modified silica–zirconia acid catalysts

Daniel J. Rosenberg and James A. Anderson*

Surface Chemistry and Catalysis Group, Division of Physical and Inorganic Chemistry, The University, Dundee, DD1 4HN Scotland, UK

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The acid sites of a series of phosphated silica–zirconia catalysts have been quantified by the combined use of FTIR and TGA and the data related to the activity of the samples for the isomerisation of but-1-ene. The catalyst series show a linear correlation indicative of constant TOF when the number of Brønsted acid sites is plotted against catalytic activity. However, this relationship only holds when the number of Lewis acid sites exceeds that of Brønsted acid sites suggesting that an optimal arrangement may involve both types of site. The TOF is less when the Lewis/Brønsted ratio falls below 1, a scenario that dominates at high Brønsted acid site densities. When this site arrangement prevails, a higher than expected cis/trans ratio is found in the isomerisation selectivity. These differences in the environment of the active Brønsted acid site may also be deduced from differences in the molar absorption coefficients of adsorbed basic probe molecules.

KEY WORDS: solid acid catalysts; molar absorption coefficients; FTIR; pyridine; phosphated catalysts.

1. Introduction

Solid acid catalysts are widely used in the petrochemicals industry and have an ever-increasing range of applications in fine chemicals synthesis. Preparation of active solid acid catalysts is often achieved by the combination of two or more oxides, which leads to the formation of acid groups otherwise absent in the individual component oxides. Further modification of the acid properties often involves the use of dopant anions with sulphate modified zirconia being the best known example [1–3]. The influence of sulphate on the acidic properties of mixed-oxides such as silica–titania [4] and silica–zirconia [5–7] has also been reported. Modification of mixed-oxides by the addition of phosphate has received less attention [8–10] although phosphated zirconia and zirconium phosphates have been widely studied [11–14]. Although phosphoric acid is a weaker acid than sulphuric acid, samples of oxide supported phosphate may show acid strengths greater than that of 100% sulphuric acid [8]. Sulphated oxide samples may suffer due to SO_3 loss when calcined at elevated temperatures [13,14] whereas loss of phosphate is less likely [8]. Additionally, and unlike its sulphated analogues, phosphated zirconia in an amorphous form has been shown to exhibit high activity for alkane isomerisation reactions [11]. In a previous study using sulphated silica–zirconia catalysts [15], the absence of a correlation between Brønsted acid site density and catalytic activity for either but-1-ene isomerisation or toluene alkylation by styrene was explained on the basis that the active site for reactions which both involve protonation of the C=C group, must involve an adjacent Brønsted and Lewis acid site pair where the latter acts to initially adsorb the vinyl group prior to protonation. To determine whether this is specific to sulphated catalysts or whether this has a wider applicability, the acid site densities for a series of phosphated silica–zirconia catalysts have been obtained using combined FTIR-TGA pyridine adsorption experiments [6,7] and the catalytic activity for but-1-ene isomerisation determined.

2. Experimental

2.1. Sample preparation

A phosphate-free and a number of phosphated 33 mol% zirconia–silica mixed oxide were prepared by modifying a method [16] described for the preparation of glasses. Tetraethyl orthosilicate, TEOS (Silibond 90 wt%) was combined with water, 1-propanol (Aldrich), as a solvent and nitric acid (Aldrich) used as a hydrolysis catalyst. The above were combined in overall molar ratios of, 1 : 1.2 : 1.5 : 0.2. The reagents were stirred for 2 h under nitrogen as a pre-hydrolysis period, after which, zirconium isopropoxide (Aldrich 70 wt%) diluted 10 : 1 in 1-propanol was added such that the molar ratio of Si : Zr was 2 : 1. After a further hour the final amount of hydrolysis water was added drop-wise, the final water : metal cation ratio was 2.6 : 1. All samples gelled within approximately 3 days. Propanol was then exchanged for ethyl acetate during a 5 h soxhlet extraction, the ethyl acetate being subsequently removed during 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 ethyl acetate was no longer detected in the effluent (ca. 5 flushes).

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*To whom correspondence should be addressed.

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Samples were then transferred to a vertically mounted tube furnace and calcined for 6 h under flowing air at 873 K. *In situ* phosphated samples were prepared in a similar manner however after 24 h mixing, the phosphoric acid was added. This methodology was employed as it was found that the addition of phosphoric acid as hydrolysis catalyst induced instant gelling leading to poorly mixed oxide. *Ex situ* phosphation involved addition of appropriate amounts of 0.01 M phosphoric acid to a pre-calcined aerogel followed by further calcination at 873 K. All samples were X-ray amorphous after calcination at 873 K. Samples are labelled as SiZr(x–y) where x indicates the mole ratio of phosphate to zirconium and y appears as *in* or *ex* depending on whether phosphate addition was by *in situ* or *ex situ* method.

2.2. Characterisation

BET surface areas of samples out-gassed *in situ* at 573 K were measured using N_2 adsorption at 77 K over a P/P_0 range of 0.02–0.2 using a multi-point Coulter SA 3100 instrument. FTIR spectra were recorded of the samples at ambient temperature at 4 cm^{-1} resolution on a Perkin Elmer Spectrum 2000. Sample pre-treatment was conducted under *in situ* conditions at the temperatures indicated in the text. Experiments were carried out in using ca. 80 mg of sample pressed into a 2.5 cm diameter discs at 0.10 tons cm^{-2}. Samples were placed in a horizontally mounted quartz transmittance IR cell connected to a conventional vacuum line fitted with both rotary and diffusion pumps, where they could be readily transferred between optical and furnace sections.

Acid site densities were determined from combined gravimetric and infra-red spectroscopic analysis of adsorbed pyridine [6]. Micro-gravimetric analyses were carried out using a PC controlled microbalance attached to a conventional vacuum line fitted with rotary and diffusion pumps. Approximately 100 mg of sample as a fragmented disc (prepared as per IR experiments, see above) was out-gassed 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 at, at least, 2 temperatures in the range 373–473 K (373, 398, 423 and 473) for 2 h while the mass was monitored continually at 3 s intervals throughout the experiment. Spectra were recorded after the initial evacuation of the sample at 573 K and then after following exposure to pyridine and out-gassing at the temperatures corresponding with those used in the gravimetric experiments.

The mass of pyridine retained by the sample at the different adsorption temperatures, in combination with the integrated areas underneath the bands due to the 19b ring vibrations of pyridine adsorbed at Lewis and Brønsted sites (ca. 1450 and 1540 cm^{-1}, respectively) at the corresponding temperatures allowed calculation of the Brønsted and Lewis absorption coefficients. By fitting this data to the equation:

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

the number of Lewis and Brønsted sites could be calculated, where n_T is 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 at each site, C_d is the cross sectional area (cm^2) of the pressed disc, ε is the molar absorption coefficient (cm μmol^{-1}) for pyridine at each site and m is the mass (g) of the pressed disc. Combined IR-gravimetric experiments were repeated between 3 and 5 times for each sample to ensure that the values obtained were reliable.

But-1-ene isomerisation was carried out over 80 mg of catalyst loaded into a fixed-bed, vertically mounted flow reactor and calcined at 573 K for 1 h. The sample was then cooled in a flow of nitrogen (90 mL min^{-1}) to 348 K at which point 1.5 mL min^{-1} but-1-ene (BOC, 99.99%) was introduced into the flow. Mass-flow control units controlled reactant gases. The sample was held at 348 K for a period which allowed four analyses to be made which involved injecting the reaction products into an on-line Perkin Elmer 8410 gas chromatograph fitted with an FID and 0.19 picric acid on carbograph column. The reaction temperature was then increased to 423 K and finally to 473 K.

3. Results and discussion

The mass of retained base can be used as a gauge of the total acidity while the proportion retained following evacuation at increasing temperatures highlights the relative strength of sites [6]. However, due to the range of acid site strengths across the samples, it was necessary to vary the out-gassing temperatures used to ensure that sufficient base was retained to minimise errors in calculating site numbers. The amount of pyridine retained after 423 K out-gassing was determined for all samples and thus may be used to compare the total number of sites across all the samples. When compared on a “per gram of catalyst” basis (table 1, column 3), the *ex situ* preparation, consistently yielded samples that retained less base than the parent non-phosphated mixed-oxide. On the other hand, modification of the preparation procedure by inclusion of phosphoric acid as a proportion of the hydrolysis catalysts was, at the lowest level of phosphate, detrimental in terms of total base capacity, but then showed a progressive increase as loading was increased. This trend was still apparent for this series (table 1, column 4) when samples were compared on a “per unit surface area” basis. On the same basis, all *ex situ* prepared samples displayed lower base capacity that the parent mixed-oxide.

Table 1
Sample characteristics and Infrared and Gravimetric data for pyridine adsorption

Sample (Si : Zr = 2 : 1)	BET area ($m^2 g^{-1}$)	Concentration[a]	Concentration[b]	[c]ε_{1540}	[c]ε_{1450}	$n_{Brønsted}$[d]	n_{Lewis}[d]
		373, 398, 423, 473	373, 398, 423, 473			373, 398, 423, 473	373, 398, 423, 473
SiZr (0)	317	– , – , 198, 111	– , – , 0.625, 0.352	0.53	1.78	– , – , 0.217, 0.096	– , – , 0.161, 0.116
SiZr (0.2-in)	360	– , – , 184, 100	– , – , 0.510, 0.280	0.76	1.04	– , – , 0.072, 0.036	– , – , 0.236, 0.133
SiZr (0.25-in)	421	– , – , 225, 129	– , – , 0.533, 0.306	0.73	1.07	– , – , 0.045, 0.023	– , – , 0.275, 0.161
SiZr (0.3-in)	338	– , – , 237, 131	– , – , 0.703, 0.388	0.56	1.06	– , – , 0.111, 0.041	– , – , 0.312, 0.193
SiZr (0.2-ex)	312	276, 206, 157, –	0.89, 0.66, 0.50, –	0.50	1.04	0.157, 0.114, 0.072, –	0.375, 0.284, 0.232, –
SiZr (0.25-ex)	340	270, – , 156, –	0.79, – , 0.46, –	0.62	1.02	0.110, – , 0.046, –	0.37, – , 0.230, –
SiZr (0.3-ex)	296	287, 219, 166, –	0.97, 0.74, 0.56, –	0.60	1.05	0.175, 0.122, 0.064, –	0.41, 0.32, 0.27, –

[a,b] Amount of pyridine retained after evacuation at 373, 398, 423 and 473 K, but based on: [a]μmol g^{-1} sample or [b]μmol m^{-2} sample.
[c] Molar absorption coefficient (cm μmol^{-1}) for adsorbed pyridine at the respective wavenumber.
[d] N^0 of acid sites per nm^2 (i.e. N^0 of pyridine molecules per nm^2 retained after evacuation at 373, 398, 423 and 473 K).

Pyridine adsorbed on the phosphate-free and phosphated mixed oxides gave absorption bands indicative of the presence of both Lewis (1450 cm^{-1}) and Brønsted (1540 cm^{-1}) forms of acidity although the relative band intensities varied from sample to sample. By combining FTIR and gravimetric measurements, molar absorption coefficients could be calculated for both forms of adsorbed species (table 1, columns 5 and 6). The values obtained may provide information on the relative proximity of adjacent acid sites, and thus provide evidence for the nature of the site itself [7]. Values for the pyridinium ion (Brønsted sites) did not, unlike the corresponding sulphated silica–zirconia samples [6,7], vary significantly across the two series of phosphated mixed-oxides (0.50–0.76 cm μmol^{-1} at 1540 cm^{-1}). Values for the Lewis bound pyridine on the phosphated samples showed an even narrower range of coefficients (1.02 to 1.07 cm μmol^{-1} at 1450 cm^{-1}) but were significantly lower than the value obtained for the phosphate-free parent mixed-oxide (Table 1) and for values obtained for silica–zirconia mixed oxides of varying mol % zirconia [17]. All calculated molar absorption coefficients were highly consistent irrespective of the out-gassing temperature range that was used to calculate the values indicating the absence of any coverage dependent behaviour and thus implying a high level of homogeneity in the nature of the acid sites present.

Determination of molar absorption coefficients for the adsorbed base allowed calculation of the surface densities of both types of acid site. Again, sites calculated on the basis of base retained at 423 K can be used to compare characteristics of all the samples. All phosphated samples, irrespective of the preparation procedure employed, showed reduced Brønsted site densities compared with the parent, phosphate-free mixed-oxide (table 1, column 7). In sharp contrast, Lewis site densities were always higher for the phosphate containing samples. In the case of the *in situ* phosphation route, an increase in Lewis acid site density accompanied an increase in the nominal phosphate content (table 1, column 8).

The catalytic activity for but-1-ene isomerisation was studied under conditions where cis and trans but-2-ene were the only reaction products (no structural isomerisation occurred). Results indicate (table 2) an absence of correlation between amount of added phosphate and catalytic activity. The selectivity expressed as the ratio of the two isomers (table 2) was fairly consistent throughout for the two series of phosphated samples, falling within the range 1.3 : 1 to 1.45 : 1 suggesting that an isomerisation mechanism prevailed which was common to all phosphated samples. Cis/trans ratios of close to one are usually taken as indicative of a Brønsted acid catalysed mechanism [18,19] where a common activated complex leads to formation of the metastable 2-butyl carbenium ion intermediate and interaction of the latter with the surface induces differences between the activation energies in the pathways leading to formation of the cis or trans but-2-ene. As these differences can be rather small (e.g. $\Delta E_a = 2.9$ kJ mol^{-1} for Mo/Al_2O_3 [19]), ratios of close to 1 are commonly observed. If the isomerisation is a purely Brønsted acid catalysed reaction, then a correlation is expected between the density of Brønsted acid sites (table 1, column 7), and the activity for the reaction (table 2) normalised on a unit

Table 2
Catalytic data for but-1-ene isomerisation at 348 K

Sample	Activity[a]	Cis/trans ratio	L/B[b]
SiZr (0)	14.23	1.85 :1	0.74
SiZr (0.2-in)	11.82	1.40 : 1	3.28
SiZr (0.25-in)	8.57	1.33 : 1	6.11
SiZr (0.3-in)	18.24	1.30 : 1	2.81
SiZr (0.2-ex)	12.00	1.45 : 1	3.22
SiZr (0.25-ex)	8.84	1.37 : 1	5.00
SiZr (0.3-ex)	10.89	1.37 : 1	4.22

[a] $\mu mol\ h^{-1}\ m^{-2}$.
[b] Lewis/Brønsted acid ratio based on pyridine retained at 423 K.

area basis. Figure 1 confirms the linear relationship (R-factor = 0.995) between the two parameters for samples from both *in situ* and *ex situ* series. The gradient of the line indicates a turn-over-frequency of 0.024 s^{-1}. The linear relationship suggests that the reaction is indeed Brønsted acid catalysed and that all sites that retained pyridinium after evacuation at 423 K were also capable of protonating but-1-ene at 348 K. This would be consistent with a hierarchy of Brønsted acidity presented for zirconia-silica aerogels [20]. Extrapolation through the y-axis would suggest that in the absence of Brønsted acid sites, there is still activity, although under similar conditions a blank run using silicon-carbide, showed no conversion. This may indicate the extent of any non-Brønsted acid catalysed reaction. The phosphate-free sample (SiZr(0)) gave data laying below the line (Figure 1) possibly suggesting that a number of the sites which retained pyridine after 423 K evacuation were either inactive or were less active for the reaction at this temperature than the sites presented on the phosphated samples.

In a previous study using equivalent silica–zirconia catalysts but which had been modified by addition of sulphate [15], the lack of correlation between Brønsted acid site density and catalytic activity for either but-1-ene isomerisation or toluene alkylation by styrene was explained on the basis that the active site involved an adjacent Brønsted and Lewis acid site pair where the latter acted to initially adsorb the vinyl group prior to protonation. At low Brønsted acid site densities (or where Lewis/Brønsted > 1), the probability of adjacent Brønsted/Lewis acid site pairs existing is high and the corresponding TOF is maximised [15]. However, as the sulphate loading was increased, pyrosulphate type moieties were formed creating additional Brønsted acid sites but at the expense of the adjacent Lewis acid sites resulting in the Lewis/Brønsted ratio falling below one. This loss of the optimum site configuration led to a decrease in the TOF despite the increase in Brønsted acid sites [15].

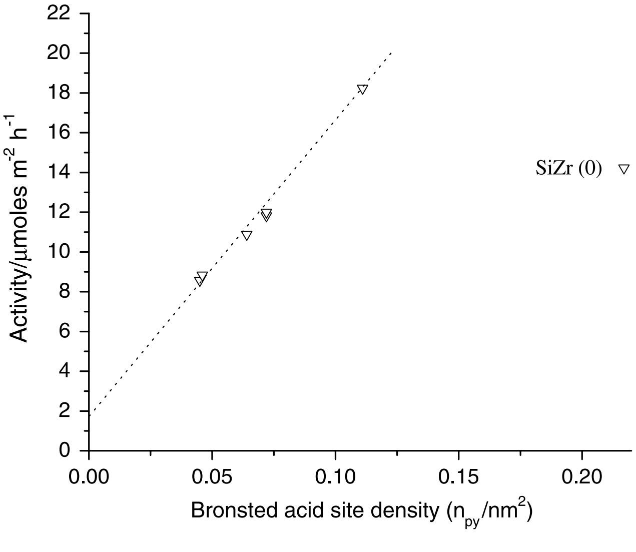

Figure 1. Relationship between activity for but-1-ene isomerisation at 348 K and Brønsted acid site density (from pyridine retained after 423 K evacuation).

The phosphate-free mixed oxide contained a greater Brønsted acid site density than any of the phosphated samples yet showed a lower TOF. This was not a consequence of acid site strengths as indicated by the data in table 1 where the relative amounts of pyridinium ion retained at 423 and 473 K may be compared. The amount of retained base at the Brønsted acid sites at the higher temperature was ca. 50% for the non-phosphated and the *in situ* phosphated series. The greater Brønsted acid site density for the phosphate-free mixed oxide was balanced by exhibiting the lowest Lewis acid site density of any of the samples (table 1) such that the Lewis/Brønsted ratio was less than one (table 2) and in accordance with previous data for sulphated silica–zirconia [15], led to low TOF. In further agreement with the predicted model for vinyl group activation [15], all of the phosphated samples had L/B ratios significantly greater than one (table 2) and thus exhibited a linear correlation between activity and number of Brønsted acid sites.

The high cis/trans ratio of 1.85 : 1 for the phosphate-free sample compared values of between 1.3 and 1.45 : 1 for the phosphated samples (table 2) may suggest that alternate factors contribute to the lower TOF of the former. However as the two isomerisation products share a common activated complex which then leads to the formation of the 2-butyl carbenium ion intermediate, then differences in the cis/trans ratio can be explained on the basis of differences in the nature of the interactions of the latter with the surface [19]. One clear justification for differences in the manner in which the intermediate interacts with the surface would be whether the active site consists of a Lewis/Brønsted acid site pair or an adjacent Brønsted acid site pair. The high cis/trans ratio of 1.85 : 1 for the phosphate-free sample may originate from the interactions experienced by the intermediate with an adjacent Brønsted acid site pair rather an adjacent Lewis/Brønsted acid site pair site present for the phosphated sample where the latter arrangement apparently leads to a greater degree of similarity in the activation energies leading to the cis and trans but-2-ene products.

In previous studies of sulphated silica–zirconia, it has been suggested that information regarding the proximity of Lewis/Brønsted acid site pair sites may be obtained from the molar absorption coefficients for adsorbed pyridine on the respective acid sites [7,15]. Data in table 1 (columns 5 and 6) show that the molar absorption coefficient for the Brønsted acid site of the anomalous sample (SiZr(0)) is in line (0.53 cm μmol^{-1}) with the value of the others, falling within the range 0.50 to 0.76 cm μmol^{-1}. However a value of 1.78 cm μmol^{-1}

at 1450 cm^{-1} is clearly at odds with the narrow range of values (1.02–1.07 cm μmol^{-1}) shown by the other samples, giving a strong indication that the environment of these sites are quite dissimilar between the two types of sample. One is tempted to relate the differences in molar absorption coefficients which result from differences in the probe molecule–surface interactions, with the different surface interactions experienced by the intermediate formed during catalytic reaction which leads [19] to changes in the extent to which cis/trans isomers are formed. In a similar way, the uniformity in the molar absorption coefficients for all the phosphated catalysts and indicative of a high degree of homogeneity in the adsorption site environment across all the samples, would also be reflected in a similarity in the surface interactions experienced by the reaction intermediate on all samples, giving rise to little variation in the cis/trans ratio of the product, as indeed was observed experimentally (table 2). A detailed analysis of the surface features of this catalyst will be forthcoming [D.J. Rosenberg *et al.*, in preparation].

4. Conclusions

A linear correlation has been obtained when the number of Brønsted acid sites, determined by FTIR of adsorbed pyridine, was plotted against catalytic activity for but-1-ene isomerisation. This correlation breaks down when the density of Brønsted acid sites becomes too high and/or when $L/B < 1$. This leads to changes in the cis/trans selectivity for the reaction that indicates changes in the environment of the active site. These changes in the local environment surrounding the active site also appear to be reflected in changes in the molar absorption coefficients for the adsorbed probe molecule.

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