Infrared Study of Water and Pyridine Adsorption on the Surface of Anhydrous Vanadyl Pyrophosphate

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Infrared spectra of vanadyl pyrophosphate contained a broad maximum at $2550-3550 \text{ cm}^{-1}$ which exchange experiments with deuterium oxide showed could be primarily attributed to residual OH-containing species in the bulk crystal lattice. However, the presence of Brønsted-acidic surface hydroxy groups was exhibited by the generation of adsorbed pyridinium ions when $(VO)_2P_2O_7$ was exposed to pyridine vapour. Pyridine was also adsorbed on Lewis-acidic surface sites, some of which were converted to Brønsted-acidic sites by the adsorption of water.

Vanadyl pyrophosphate $(VO)_{2}P_{2}O_{7}$ has been shown to be an important constituent of vanadium-phosphorus mixed-oxide catalysts which are active for the oxidation of butane¹ or but-1-ene^{2, 3} to maleic anhydride. Temperature-programmed desorption studies of the interactions between but-1-ene and vanadium-phosphorus mixed-oxide catalysts led to the conclusion that $(VO)_{a}P_{a}O_{z}$ was responsible for the oxidation of butene to butadiene and crotonaldehyde, which were subsequently converted to maleic anhydride via catalysis involving β -VOPO₄.³ The t.p.d. data suggested that five types of surface centre existed on active catalyst, each type of centre interacting with but-1-ene to form a particular surface complex which gave characteristic desorption products at elevated temperatures. A peak in the t.p.d. curve at 453 K corresponded to the desorption of but-1-ene and but-2-enes. Active sites responsible for the isomerization reaction may be Brønsted-acidic surface hydroxy groups, which interact with but-1-ene to form an adsorbed intermediate carbocation. An alternative would be that incompletely coordinated exposed vanadium cations (Lewis-acidic surface sites) provided centres for the adsorption of but-1-ene as a π -allyl intermediate. Ai and Suzuki⁴ have shown that the selectivity of vanadium-phosphorus mixed-oxide catalysts is influenced by surface acidity. The present infrared study of the adsorption of water and pyridine on vanadyl pyrophosphate was undertaken to probe the existence of surface hydroxy groups and Brønsted- and Lewis-acidic sites⁵ on the surface of pure $(VO)_{0}P_{0}O_{2}$.

Experimental

Vanadyl pyrophosphate was prepared by the reaction of vanadium pentoxide and orthophosphoric acid in strongly acidic solution and subsequent thermal activation of the reaction product in vacuum. The X.r.d. pattern and infrared spectrum of the product were consistent with data for $(VO)_2P_2O_7$.² Samples of *ca*. 55 mg (surface area 11 m² g⁻¹) were compressed (3.5 ton) into self-supporting discs (diameter 25 mm) and mounted in a conventional infrared cell fitted with fluorite windows and an external furnace⁶ and glassblown to a vacuum apparatus capable of maintaining a dynamic vacuum of *ca*. 10⁻⁴ N m⁻². Discs were heated at 673 or 713 K for 17 h before spectroscopic study of the adsorption of water or pyridine. Spectra were recorded using a Perkin–Elmer 580A spectrophotometer.

Water was ion-exchanged and triply distilled, once from alkaline potassium permanganate and twice from itself, all under nitrogen. Water and deuterium oxide

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Fig. 1. Spectra of $(VO)_2P_2O_7$ after evacuation (17 h, 673 K) and (a)-(d) evacuation (ca. 300 K, 1 h) following exposure to water vapour (ca. 300 K) at pressures of (a) 0, (b) 57, (c) 114 and (d) 228 N m⁻²; (e)-(f) exposure to water vapour (228 N m⁻², ca. 300 K) and evacuation at (e) 493 and (f) 693 K.

(Fluorochem $\ge 99.8\%$) stored in bulbs on the vacuum line were freed from permanent gases by series of freeze-thaw cycles. Pyridine ($\ge 99.5\%$) was purified by double distillation from solid KOH.

Results

The infrared spectrum of $(VO)_2P_2O_7$ exhibits a series of bands in the 700–1300 cm⁻¹ spectral region which may be assigned to vibrations of VO^{2+} and $P_2O_7^{2-}$ ions in the bulk phase.² Spectra of pressed discs contained a broad band envelope in the range 2500–3550 cm⁻¹ [fig. 1(*a*)] due to OH-stretching vibrations of trace amounts of water or OH-containing species retained after the vacuum decomposition of the precursor, $(VO)_2P_2O_7 \cdot 2H_2O$. Exposure of discs to water vapour enhanced the intensity of absorption in the 2550–3700 cm⁻¹ region and led to the appearance of a maximum at 1620 cm⁻¹ due to the deformation vibrations of non-dissociatively adsorbed water molecules [fig. 1(*b*)–(*d*)]. The adsorbed water was not desorbed by evacuation at the ambient temperature in the sample beam of the spectrophotometer [fig. 1(*d*)] and some water was retained even after evacuation at 493 K [fig. 1(*e*)].

Exchange experiments involving deuterium oxide were carried out to distinguish between bulk and surface OH-containing species. The broad band envelope at 2550–3550 cm⁻¹ [fig. 1(*a*)] in spectra of $(VO)_2P_2O_7$ before the adsorption of water is predominantly ascribed to bulk species because the envelope was retained in spectra after exposure of discs to excess deuterium oxide vapour [fig. 2(*c*)]. Adsorbed deuterium oxide gave a broad maximum centred at 2600 cm⁻¹, equivalent to the maximum at *ca*. 3500 cm⁻¹ for adsorbed water. A sequence of alternate treatments with water and deuterium oxide established the complete reversibility of the exchange process [fig. 2(*c*) and (*d*)]. A final treatment with water gave a closely similar spectrum [fig. 2(*d*)] to that

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Fig. 2. Spectra of $(VO)_2P_2O_7$ after evacuation (17 h, 673 K), exposure to excess water vapour (*ca.* 300 K) and evacuation at (*a*) *ca.* 300 and (*b*) 693 K, (*c*) after subsequent exposure to excess D_2O vapour and evacuation, then excess H_2O vapour and evacuation and finally excess D_2O vapour and evacuation (all at *ca.* 300 K), (*d*) after subsequent re-exchange with H_2O and evacuation at *ca.* 300 K.

[fig. 2(a)] initially recorded after exposure of $(VO)_2P_2O_7$ to water vapour and evacuation at *ca*. 300 K.

Spectra of $(VO)_{2}P_{2}O_{7}$ after heat treatment in vacuum at 713 K and exposure to pyridine vapour at ambient temperature are shown in fig. 3A. Infrared bands at 1610, 1575 and 1450 cm^{-1} for low pressures of pyridine may be assigned to vibrations of pyridine molecules⁷ adsorbed through coordinative interaction with Lewis-acidic surface sites.⁸⁻¹¹ Th concomitant appearance of a weak band at 1540 cm⁻¹ suggested the presence of some Brønsted-acidic sites on the $(VO)_2P_2O_7$ surface. A band in spectra at 1490 cm⁻¹ must have contained contributions due to vibrations of both pyridinium ions and coordinatively adsorbed pyridine molecules.^{8, 10, 11} Spectra of discs in contact with high vapour pressures of pyridine [fig. 3A(d)-(f)] contained no additional features due to adsorbed pyridine, but exhibited additional bands at 1587 and 1440 cm⁻¹, in particular, due to vibrations of pyridine molecules in the vapour phase [fig. 3A(d)]. Removal of pyridine vapour by evacuation with the sample at room temperature gave a spectrum [fig. 3B(c)] showing the retention of both adsorbed pyridine on Lewis-acidic sites and adsorbed pyridinium ions. Subsequent evacuation at 323 K had little effect, but the extents of desorption of both species progressively increased as the sample temperature was raised during evacuation of the infrared cell until at 673 K desorption was complete (fig. 3B).

Water vapour was added to a $(VO)_2P_2O_7$ disc on to which pyridine had been preadsorbed in order to test for the conversion of surface Lewis-acidic sites to Brønstedacidic sites in the presence of adsorbed water. Strong evidence for conversion was provided by the observed decrease in the intensity of the maximum at 1450 cm⁻¹ and the parallel increase in intensity of the band at 1540 cm⁻¹ as the surface concentration of

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Fig. 3. A, Spectra of $(VO)_2P_2O_7$ after evacuation (17 h, 713 K) and exposure to pyridine vapour (*ca.* 300 K) at pressures of (*a*) 0, (*b*) 0.18, (*c*) 0.36, (*d*) 0.54, (*e*) 1.17 and (*f*) 1.35 kN m⁻². (*g*) Spectrum of pyridine vapour (1.35 kN m⁻²). B, (*a*) as A(*a*), (*b*) as A(*f*), (*c*)–(*i*) after subsequent evacuation (*c*) at 293 K (17 h), followed by 1 h at (*d*) 323, (*e*) 393, (*f*) 463, (*g*) 543, (*h*) 593 and (*i*) 673 K.

adsorbed water was increased (fig. 4A). Adsorbed water gave a broad maximum at 1620 cm^{-1} which obscured bands in the $1570-1670 \text{ cm}^{-1}$ region due to adsorbed pyridine. The reversal [fig. 4A(b) and (f)] of the relative intensities of the maxima at 1450 and 1490 cm⁻¹ confirmed that the latter contained contributions due to pyridine interacting with both Lewis- and Brønsted-acidic sites. Subsequent thermal activation in vacuum led to the desorption of both water and pyridine (fig. 4B) at temperatures consistent with those observed in the separate experiments with water (fig. 1) and pyridine (fig. 3) alone.

The addition of deuterium oxide to coadsorbed water and pyridine on $(VO)_2P_2O_7$ decreased the intensity of the band at 1620 cm⁻¹ due to the bending vibrations of water molecules and hence revealed the narrower band at 1610 cm⁻¹ [fig. 4C(d)-(f)] due to a vibration of pyridine adsorbed on Lewis-acidic surface sites. The exchange of adsorbed water by adsorbed deuterium oxide caused the disappearance of the weak band at 1540 cm⁻¹ ascribed to pyridinium ions (pyH⁺) because of the concomitant conversion of the latter to their deuterated analogue pyD⁺. The effects of the H/D-isotope exchange were reversed by the reintroduction of water to the infrared cell [fig. 4C(g)]. The absence of the band at 1540 cm⁻¹ for (VO)₂P₂O₇ with coadsorbed pyridine and deuterium oxide was further confirmed by admission of deuterium oxide to a pyridine-covered surface, which had not also been exposed to water (fig. 5A). In accordance with the present conclusions, the spectrum of a solution of pyD⁺Cl⁻ in deuterium oxide contained no band at 1540 cm⁻¹ [fig. 5A(g)], at which position there was a strong adsorption maximum in the spectrum of pyH⁺Cl⁻ in water [fig. 5A(h)].¹²

The spectrum of pyD^+Cl^- contained a strong band at 1483 cm⁻¹ which was responsible for the growth in intensity and small shift to lower wavenumbers of the band at

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Fig. 4. A, Spectra of (VO)₂P₂O₇ after (a) evacuation (17 h, 673 K), (b) exposure to pyridine vapour (0.54 kN m⁻²) and evacuation (ca. 300 K), and subsequent exposure to water vapour (ca. 300 K) at pressures of (c) 0.19, (d) 0.38, (e) 0.67 and (f) 1.25 kN m⁻². B, (a) as A(a), (b) as A(f), (c)–(h) after subsequent evacuation (1 h) at (c) ca. 300, (d) 383, (e) 433, (f) 533, (g) 603 and (h) 673 K. C, (a) as A(a), (b) after subsequent evacuation (1 h, ca. 300 K) and exposure to pyridine followed by water [cf. spectrum A(f)], (c)–(f) after evacuation (1 h, ca. 300 K) following subsequent exposure to D₂O vapour at pressures of (c) 96, (d) 192, (e) 384 and (f) 768 kN m⁻² and (g) after re-exchange with H₂O (125 kN m⁻²) followed by evacuation (1 h, ca. 300 K).

1490 cm⁻¹ [fig. 5A(b)] as pyD⁺ ions were generated on the $(VO)_2P_2O_7$ surface by the adsorption of deuterium oxide [fig. 5A(b)-(f)]. A concurrent weakening of the maximum at 1610 cm⁻¹ accompanied the conversion of pyridine molecules at Lewis-acidic sites to pyD⁺ ions. Desorption of pyridine from Lewis- and Brønsted-acidic surface sites was complete after evacuation of $(VO)_2P_2O_7$ at 713 K (fig. 5B).

Discussion

The existence of surface hydroxy groups on $(VO)_2P_2O_7$ which had been heated at 713 K in vacuum was shown by the appearance of the band at 1540 cm⁻¹ in spectra of adsorbed pyridine. The absence of narrow infrared bands due to OH-stretching vibrations suggests that the hydroxy groups were involved in hydrogen-bonding interactions, probably with adjacent surface phosphate ions. Contributions to the infrared spectra due to the hydroxy groups were obscured by the broad maximum at 2550–3550 cm⁻¹, primarily attributed to bulk species, and were too small and diffuse to be detectable by the deuterium-exchange experiments. Isolated surface P–OH groups, not involved in hydrogen bonding, would have been expected to give a narrow infrared band at *ca*. 3700 cm⁻¹.¹³

The surface of $(VO)_2P_2O_7$ is Brønsted-acidic after heat treatment at temperatures typical of those used in the catalytic oxidation of butane or butenes to maleic anhydride. Brønsted-acid sites could therefore be involved in the catalytic process, possibly at the

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Fig. 5. A, Spectra of (VO)₂P₂O₇ after (a) evacuation (17 h, 673 K; 17 h, ca. 300 K), (b) exposure to pyridine vapour (0.54 kN m⁻²) and evacuation (ca. 300 K), (c)–(f) subsequent contact with D₂O vapour at pressures of (c) 96, (d) 192, (e) 288 and (f) 384 kN m⁻². (g) Spectrum of a solution of pyridine (22 vol %) in concentrated DCl in D₂O, (h) spectrum of pyridine (22 vol %) in concentrated DCl in D₂O, (h) spectrum of pyridine (22 vol %) in concentrated aqueous HCl. B, (a) as A(a), (b)–(h) disc treated as for spectrum A(f) followed by evacuation (1 h) at (b) 293, (c) 323, (d) 443, (e) 553, (f) 603, (g) 673 and (h) 713 K.

early stage of butene isomerization.³ An alternative source of Brønsted acidity to surface hydroxy groups would be non-dissociatively adsorbed water molecules coordinatively bound to exposed vanadium cations. Intensities of the infrared band at 1620 cm⁻¹ showed that water could be the source of Brønsted acidity at least up to 493 K, but that heating $(VO)_2P_2O_7$ at 693 K left an undetectable level of retained surface water.

Analysis of the intensities of the bands at 1540, 1490 and 1450 cm⁻¹ in spectra of adsorbed pyridine have enabled the relative numbers of Lewis and Brønsted sites on $(VO)_2P_2O_7$ to be estimated. Using a formula containing the intensities of the bands at 1490 and 1450 cm⁻¹ [ref. (8)] gives a value of 2.1 times as many Lewis sites as Brønsted sites on $(VO)_2P_2O_7$ which had been heated at 673 K in vacuum. Subsequent saturation with water at room temperature resulted in the conversion of Lewis-acidic to Brønsted-acidic sites and the surface concentration of the former fell to 0.7 times that of the latter. An alternative method of calculation using the intensities of the maxima at 1540 and 1450 cm^{-110, 11} gave a value of ([L]/[B]) of 2.0 for the initial surface and 0.5 after the adsorption of water. Lewis sites on $(VO)_2P_2O_7$ heated in vacuum are probably exposed V⁴⁺ cations.

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