J. Chem. Soc., Faraday Trans. 1, 1987, **83**, 853–864

A Fourier-transform Infrared and Catalytic Study of the Evolution of the Surface Acidity of Zirconium Phosphate following Heat Treatment

Guido Busca and Vincenzo Lorenzelli*
Istituto di Chimica, Facoltà di Ingegneria, Università, Fiera del Mare, Pad. D, 16129 Genova, Italy

Paola Galli and Aldo La Ginestra
Dipartimento di Chimica, Università, P. le Aldo Moro 5, 00185 Roma, Italy

Pasquale Patrono
Istituto di Metodologie Avanzate Inorganiche, CNR, Area di Ricerca di Roma C.P.10, 00016 Monterotondo Scalo, Roma, Italy

The surface acidity of zirconium phosphate at different stages of dehydration and heat treatments has been studied by Fourier-transform infrared spectroscopy of adsorbed pyridine, acetonitrile and acetone and by catalytic activity in the isomerization of but-1-ene. Brönsted-acidic surface POH and $P(OH)_2$ groups are identified [ν(OH) = 3670–3660 and 3600 cm^{-1}, respectively] whose strength increases slightly on bulk dehydration. They are thought to be responsible for the activity in but-1-ene isomerization, which also increases during condensation to pyrophosphate. Lewis-acidic sites of medium-high strength have also been found, and responsible for the formation of chemisorbed forms of pyridine (ν_{8a} = 1610 cm^{-1}), acetonitrile [ν(CN) Fermi resonance doublet at 2322 and 2295 cm^{-1}] and acetone [ν(CO) 1684 cm^{-1}]. Surface ZrOH groups are also detected on the layered ZrP_2O_7 surface. The results illustrate the role of exposed planes, both parallel and perpendicular to the layered structure.

Zirconium acid phosphate, $Zr(HPO_4)_2 \cdot H_2O$, is now the object of research owing to its activity as an inorganic ion-exchanger[1] and its thermal behaviour, which produces several different crystal phases.[2–4] It is one of the better known compounds of the class of isostructural layered phosphates and arsenates of tetravalent metals (Ti, Zr, Sn and Ge),[5] for which interesting applications are being studied, either as such or in their ion-exchanged forms.

These compounds also exhibit interesting activities in heterogeneously acid-catalysed reactions.[6–8] The surface acidity of zirconium phosphate has been the object of previous studies, mainly based on titration methods[6, 9] and on catalytic measurements.[6–10] However, its surface characterization is not complete, the nature and behaviour of the surface-acidic sites still being largely unknown. The present paper reports the results of a study of the surface acidity of $Zr(HPO_4)_2 \cdot H_2O$ after different dehydration pretreatments performed using infrared spectroscopy of adsorbed probe molecules and by examining the catalytic behaviour in test reactions.

Experimental

Crystalline α-zirconium acid phosphate hydrate was prepared starting from $ZrOCl_2 \cdot 8H_2O$(Merck), by refluxing the amorphous product in 10 mol dm^{-3} H_3PO_4 for

100 h.[11] This product was subsequently heated in flowing O_2 at different temperatures for 12 h to obtain the various dehydration products (see text) used in the catalytic tests.

Fourier-transform infrared spectra were recorded in the region 4800–500 cm^{-1} with a Nicolet MX1 Fourier-transform spectrometer, equipped with conventional gas manipulation/evacuation ramps and heatable i.r. cells. For the characterization of the different crystal phases, KBr pressed discs were used. Experiments on dehydration under vacuum and on the adsorption of probe molecules were carried out using pressed discs of the pure zirconium phosphate powder. Catalytic measurements were performed as reported elsewhere.[10]

Results

Infrared Characterization of the Crystal Phases

The spectra (KBr pressed discs) of the different crystal phases resulting from heat treatments in the temperature range 290–1050 K, are reported in fig. 1. In oxygen[2–4] the zirconium bis(hydrogenphosphate)monohydrate (hereafter denoted α-ZrP·H_2O), characterized by an interlayer distance $d_{002} = 7.56$ Å, transforms near 450 K into the corresponding anhydrous form α'-ZrP ($d_{002} = 7.43$ Å), which shows a reversible phase transition to another anhydrous form α''-ZrP ($d_{002} = 6.8$ Å) near 470 K. Heat treatment between 770 and 1100 K produces the layered pyrophosphate, L-ZrP_2O_7, characterized by $d_{002} = 6.1$–6.3 Å, which later transforms into the more stable cubic form, α-ZrP_2O_7.

The spectrum of the starting sample α-ZrP·H_2O is reported in fig. 1(*a*). It corresponds to one previously published[12] that has been interpreted mainly on the basis of a comparison with the spectrum of the room-temperature anhydrous form, α'-ZrP. In particular, the pair of sharp bands at 3589 and 3512 cm^{-1} has been attributed to the asymmetric OH stretching of the water molecules, split according to site asymmetry.[12] The broad band at 3170 cm^{-1} has been assigned to the corresponding symmetric stretch, while the deformation is clearly connected to the sharp band, asymmetric towards higher frequencies, at 1622 cm^{-1}. All such features, together with a band at 660 cm^{-1} that is probably due to a librational mode of water, are absent in the spectrum of α'-ZrP [fig. 1(*b*)]. Accordingly, the broad band near 3300 cm^{-1}, the shoulder near 1250 cm^{-1}, the sharp weak band at 965 cm^{-1} and the relatively intense band near 600 cm^{-1} characterize the POH groups of α-ZrP·H_2O (OH stretching, POH in-plane deformation, PO stretching and POH out-of-plane deformation, respectively).[13, 14] In the spectrum of α'-ZrP such bands are observable, at 3420 and 3300 cm^{-1} (slightly split and broad), near 1200 cm^{-1} (not well resolved), at 930 cm^{-1} and at 610 cm^{-1}, respectively. However, in the spectrum of α''-ZrP [recorded at 500 K, fig. 1(*c*)] two sharp bands are evident at 3665 and 3565 cm^{-1} that must necessarily be assigned to a splitting of the ν(OH) band of non-hydrogen-bonded hydrogenphosphate groups. All other features [including PO_3 stretches at 1150 (sh), 1060, 1045, 1005 and 990 cm^{-1} and PO_3 deformations at 530 cm^{-1}] are substantially analogous in the spectra of both forms of anhydrous $Zr(HPO_4)_2$. In spite of the shorter interlayer distance, the ν(OH) frequencies indicate that the POH groups are not interacting in the higher-temperature form of α-$Zr(HPO_4)_2$, while they are involved in some kind of weak hydrogen bonding in the low-temperature, higher-interlayer-distance form. This may be connected with the relatively lower crystallinity of the low-temperature form. In any case, the presence of two relatively sharp ν(OH) bands above 3560 cm^{-1} in the spectrum of $Zr(HPO_4)_2$ at 500 K parallels the detection of two sharp bands at 3598 and 3512 cm^{-1} in the spectrum of the hydrated compound due to ν_{as}(OH) of water of crystallization. So, alternative assignments may be proposed to two different types of POH groups, as are determined in the crystal structure of the hydrated compound,[15] or to coupling of equivalent POH groups. In any case, the high value of ν(OH) and the low values of the corresponding POH in-plane and out-of-plane

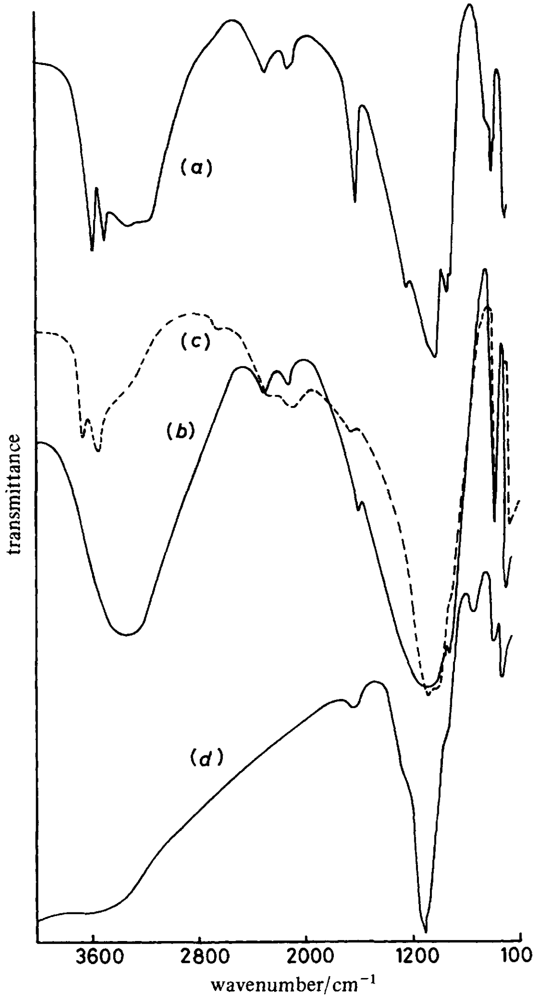

Fig. 1. Fourier-transform infrared spectra (KBr pressed discs) of (*a*) α-ZrP·H_2O, (*b*) α′-ZrP (recorded at 300 K), (*c*) α″-ZrP (recorded at 500 K) and (*d*) L-ZrP_2O_7.

deformations confirm that in layered zirconium hydrogenphosphates such groups are involved in very weak interlayer interactions,[13, 14] as also observed in the case of layered $VO(HPO_4)_2 \cdot 0.5H_2O$.[16] The spectrum of the layered pyrophosphate L-ZrP_2O_7 [fig. 1(*d*)] shows a complex absorption with unresolved components at 1270, 1110 (very strong) and 1050 cm^{-1} [$\nu(PO_3)$], 960 cm^{-1} [$\nu_{as}(POP)$], a weaker band at 750 cm^{-1} [$\nu_{sym}(POP)$] and near 600 and 520 cm^{-1} (PO_3 deformations). This spectrum is markedly different from that of the cubic form,[17] particularly concerning the relative intensities and the resolution. To study the dehydration treatments *in vacuo* and the adsorption of probe molecules, pressed discs of the pure powder must be used, to avoid contamination by the KBr binding material. However, as expected, such samples are opaque in the region 3600–2900 cm^{-1} and below 1300 cm^{-1}, where very intense skeletal $\nu(OH)$ and $\nu(PO)$–$\delta(POH)$ bands fall, respectively. Only in the former region does transmittance appear when decomposition to L-ZrP_2O_7 begins, as shown below. Thus pressed discs of the pure

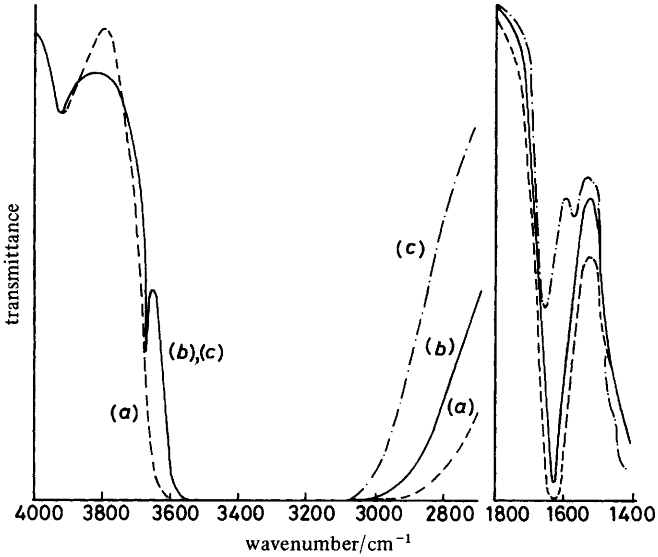

Fig. 2. Fourier-transform infrared spectra of an α-ZrP·H_2O pressed disc after evacuation at (*a*) room temperature, (*b*) 370 K and (*c*) 470 K (all recorded at room temperature).

powder do not permit monitoring of the bulk state of the sample through examination of the fundamental skeletal frequencies. However, as has been shown on other metal phosphates,[16, 18] overtone and combination bands, less intense and weakly detectable in KBr but well evident in discs of the pure powder, may be useful in deducing the bulk structure under experimental conditions. Accordingly, above 3600 cm^{-1} two absorptions (4560–4500 and 3920 cm^{-1}) are present in the spectra of both the hydrated and anhydrous hydrogenphosphates, but disappear completely after decomposition to L-ZrP_2O_7.

Such bands may be assigned to combinations of the ν(OH) fundamental with the in-plane and out-of-plane δ(POH) deformations. Multiple absorptions in the region 3000–1300 cm^{-1}, are present, but slightly different, both on α′-ZrP and on L-ZrP_2O_7 owing to combinations and overtones of the PO stretching vibrations and POH deformations.

Infrared Study of Bulk and Surface Dehydration by Heating *in vacuo*

Thermogravimetric studies previously published[4, 5] indicate, according to X.r.d. analyses of the bulk structures, that different dehydration processes due to desorption of water from the external surface, loss of crystallization water, condensation of hydrogen phosphate ions to produce pyrophosphate ions, loss of trapped water and surface dehydration, take place successively, but practically overlap depending on morphological factors such as the degree of crystallinity and crystal size, and on experimental factors such as the heating rate and water-vapour external pressure. To try to distinguish such processes, we have followed spectroscopically the dehydration of $Zr(HPO_4)_2\cdot H_2O$ by heating *in situ* under evacuation.

Evacuation at temperatures up to 370 K primarily causes the following spectral changes (fig. 2): (*a*) the appearance of a weak sharp band at 3670 cm^{-1} on the higher-frequency side of the bulk ν(OH) absorption; (*b*) a sharpening of the δ(OH_2) band at 1620 cm^{-1}. The band at 3670 cm^{-1} is clearly surface-sensitive, as it disappears on the adsorption of basic molecules. Both such effects indicate the desorption of external-shell water, which makes free surface hydroxy groups and leaves only ‘bulk’ water molecules.

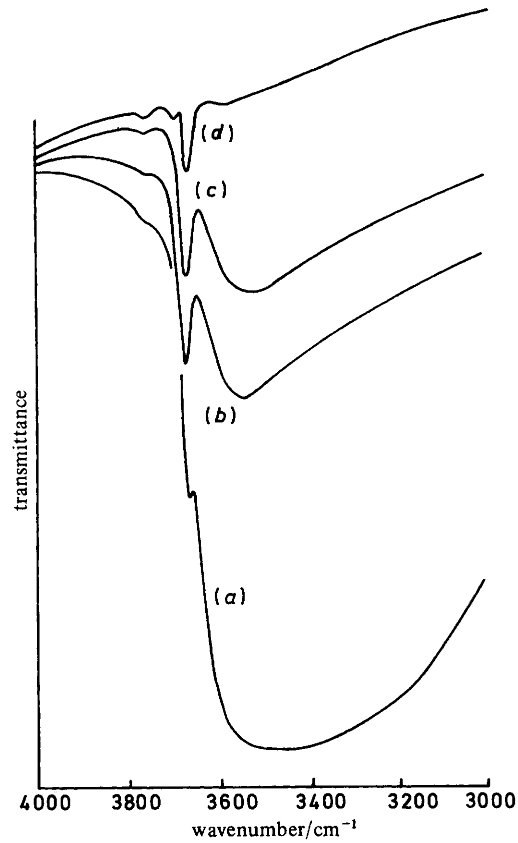

Fig. 3. Fourier-transform infrared spectra of an α-ZrP·H_2O pressed disc after evacuation at (*a*) 820, (*b*) 900, (*c*) 970 and (*d*) 1050 K.

The band at 3670 cm^{-1} looks very similar to those observed on the surfaces of other phosphate compounds such as $AlPO_4$,[19] BPO_4[20] and $(VO)_2P_2O_7$,[21] and may be assigned to ν(OH) of hydrogenphosphate groups on the external surface. Evacuation at temperatures intermediate between 370 and 470 K causes the disappearance of the band at 1622 cm^{-1}, leaving two bulk combination or overtone bands (surface-insensitive) at 1660 and 1590 cm^{-1} [fig. 2(*c*)]. The relative intensity of the band at 3670 cm^{-1} increases further. Simultaneously the lower limit of the black-out region due to bulk ν(OH) shifts from 2900 to 3080 cm^{-1}. All these features are consistent with the loss of bulk water to produce α'-ZrP, as already known.[2, 3]

Further evacuation at temperatures up to 820 K causes progressive changes in the overall spectrum in which the features of α'-ZrP are progressively substituted by those of L-ZrP_2O_7. Complete cavity dehydration is ended in our experimental conditions at 820 K, as shown by the already complete transformation of the bulk overtone bands cited previously. Further heat treatment under evacuation up to 1050 K only affects the 3800–3000 cm^{-1} region (fig. 3). A very broad and intense ν(OH) band in the 3550–3250 cm^{-1} region is still present on the sample treated at 820 K, together with that at 3664 cm^{-1} (slightly shifted to lower frequency with respect to the previous value of 3670 cm^{-1}) already assigned to free surface POH groups. The broader band is clearly connected with hydrogen-bonded POH groups.

Evacuation at temperatures up to 1050 K causes the progressive complete disappear-

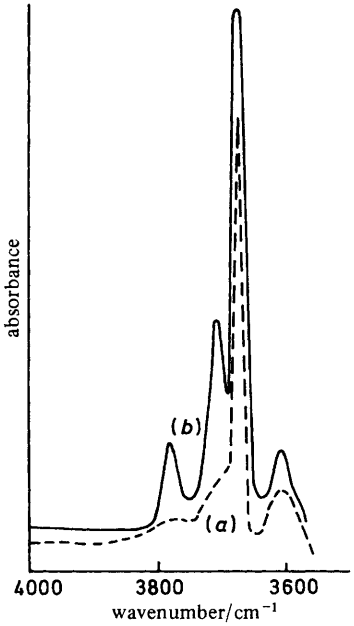

Fig. 4. Fourier-transform infrared spectra of α-ZrP·H_2O pressed discs activated *in vacuo* at (*a*) 820 and (*b*) 1050 K, in the ν(OH) region. Such spectra are obtained as ratios of the spectra after and before contact with high acetonitrile pressure, and represent bands that disappear in contact with acetonitrile.

ance of the broad band at lower frequencies, a partial decrease of the 3660 cm^{-1} band (that also broadens slightly) and the clear appearance of two other weak bands at 3770 and 3700 cm^{-1}. Assignments of such bands to ν(PO—H) seems unlikely. They are probably due to ν(ZrO—H), according to their similarity with the ν(OH) bands of surface hydroxyls of ZrO_2 observed at 3780 and 3680 cm^{-1}.[22]

Moreover, the ratioed spectra obtained after adsorption of bases at all dehydration stages clearly indicate the presence of another sharp component at 3600 cm^{-1} (fig. 4) that may be tentatively assigned, according to previous data,[20, 21] to geminal $P(OH)_2$ groups. Thus a study of the dehydration under evacuation of α-ZrP·H_2O leads to the identification of the following steps: (*a*) desorption of external-shell water between 300 and 370 K; (*b*) loss of cavity water between 370 and 470 K; (*c*) condensation of hydrogenphosphate groups to produce layered pyrophosphate, occurring prevalently between 670 and 820 K; (*d*) completion of L-ZrP_2O_7 dehydration between 820 and 1050 K. The study of the dehydration *in vacuo* has also allowed us to detect directly the surface sites that may potentially act as Brönsted-acid sites; they are: (*a*) free surface POH groups, present at all dehydration stages, whose ν(OH) frequency shifts slightly during bulk dehydration from 3670 to 3660 cm^{-1}; (*b*) geminal surface $P(OH)_2$ groups [ν(OH) 3600 cm^{-1}], also present at all dehydration stages; (*c*) surface ZrOH groups in two forms [ν(OH) 3770 and 3700 cm^{-1}], evident in particular in L-ZrP_2O_7; (*d*) hydrogen-bonded POH groups [ν(OH) 3550–3250 cm^{-1}], whose location on the surface or in the interlayer region is still unclear; these disappear on evacuation at 1050 K.

Infrared Study of the Adsorption of Basic Probe Molecules

The nature and strength of the surface acid sites has been studied following the adsorption of the basic molecules pyridine, acetone and acetonitrile on the better

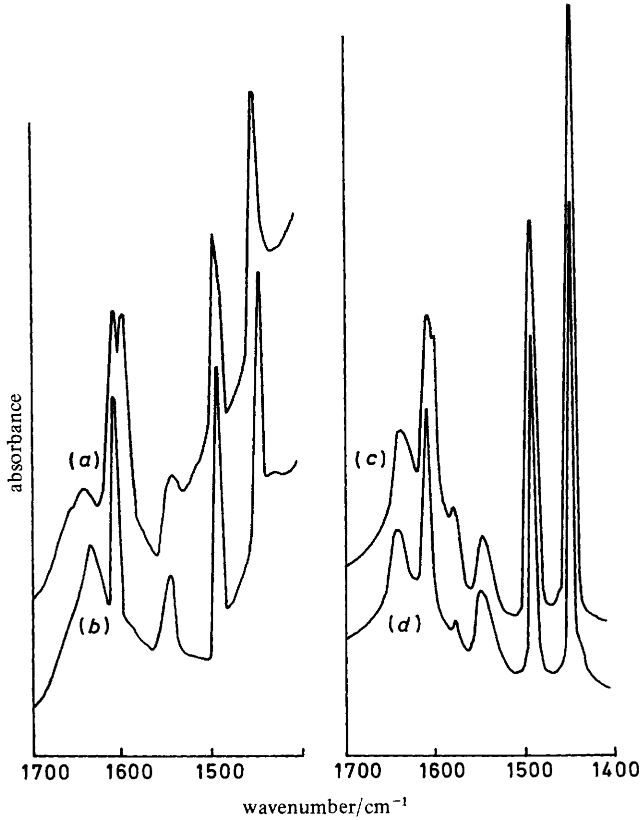

Fig. 5. Fourier-transform infrared spectra of pyridine adsorbed on α-ZrP·H_2O pressed discs activated *in vacuo* at (*a*), (*b*) 473 K (α'-ZrP) and (*c*), (*d*) 1050 K (L-ZrP_2O_7) and evacuated at (*a*), (*c*) room temperature and (*b*), (*d*) 420 K.

characterized samples, obtained by dehydration at 470 K (α'—ZrP) and at 820, 900 and 1050 K (L-ZrP_2O_7).

The spectra of pyridine adsorbed on samples treated at 470 K (α'-ZrP) and at 1050 K (L-ZrP_2O_7) are compared in fig. 5. In both cases bands are observed at 1640 and 1545 cm^{-1} typical of pyridinium cations. This result confirms the presence of Brönsted sites, already shown by catalytic measurements. The Brönsted acidity is probably connected with POH surface groups. In fact, pyridine protonation at room temperature has been observed on several phosphate catalysts.[19-21] The previously observed ZrOH groups are probably much less acidic, being unable to protonate pyridine at room temperature, as observed on zirconia.[23] It seems reasonable that geminal $P(OH)_2$ groups also participate in Brönsted acidity.

However, bands that are certainly due to chemisorbed pyridine are also evident near 1600, 1570, 1490 and 1445 cm^{-1}. This result contradicts previous reports by Hattori *et al.*[9] that only the protonated form is observed. The more sensitive vibrational mode of pyridine (ν_{8a}) in both cases appears clearly split into two components at 1610 and 1600 cm^{-1} after evacuation at room temperature. The lower-frequency band characterizes a species more weakly held, as expected, being desorbed by evacuation at 420 K. However, upon evacuation the corresponding ν_{8a} vibration shifts to 1604 cm^{-1}. Such a value, and the stability of such a species following evacuation at room temperature, rule

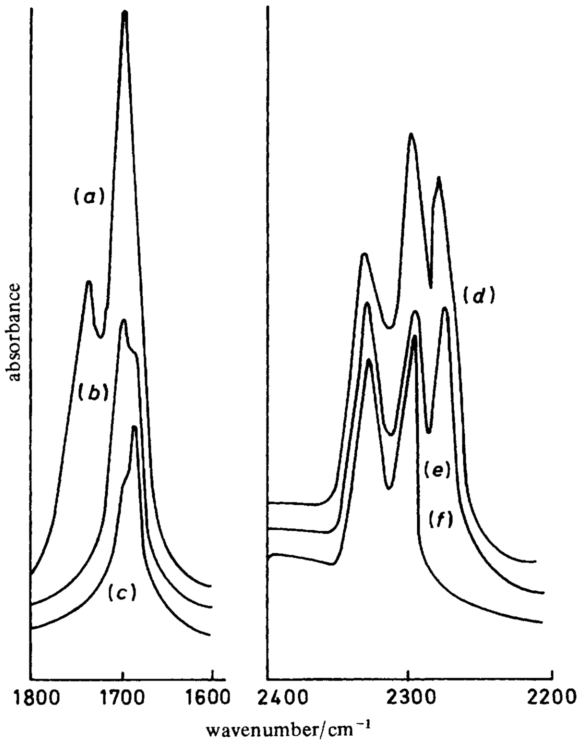

Fig. 6. Fourier-transform infrared spectra of acetone (*a*)–(*c*) and acetonitrile (*d*)–(*f*) adsorbed on L-ZrP_2O_7. Acetone was evacuated at room temperature for (*a*) 5 min, (*b*) 30 min and (*c*) 1 h. Acetonitrile was evacuated at (*d*) room temperature for 30 min, (*e*) 400 K for 10 min and (*f*) 473 K for 10 min.

out a possible assignment to hydrogen-bonded pyridine. It is thus assigned to a species chemisorbed on relatively weak Lewis sites. The higher-frequency band is certainly connected to a species chemisorbed on Lewis-acid sites of medium strength. The only reasonable assignment for such a site is to a coordinatively unsaturated exposed Zr^{4+} cation. For comparison we note that on ZrO_2 Lewis sites interact with pyridine, producing a chemisorbed species characterized by a ν_{8a} vibration at 1608 cm^{-1} if evacuation is carried out at 570 K; this shifts to 1600 cm^{-1} on samples evacuated at 770 K.[21] Thus the more strongly bonded species clearly show the presence, on the surfaces of both α'-ZrP and L-ZrP_2O_7, of exposed zirconium cations having a stronger Lewis acidity than those of the zirconia surface, probably connected with the lower basicity of the hydrogenphosphate and pyrophosphate ions with respect to the oxide ions. The weaker Lewis sites we observe are probably due to cations having a lower extent of coordinative unsaturation.

The spectra of adsorbed acetone and acetonitrile confirm the presence, at all stages of dehydration without relevant changes, of Lewis-acid sites (fig. 6). In addition to the band placed near 1735 cm^{-1}, due to very weakly adsorbed acetone, two bands due to species having different stabilities are observed at 1700 cm^{-1} (hydrogen-bonded or chemisorbed on the weaker Lewis site) and at 1684 cm^{-} (chemisorbed on the stronger site). The last value confirms the medium-high strength of the stronger Lewis sites on zirconium phosphates.

The spectra of adsorbed acetonitrile on all samples show at low coverages a pair of

Table 1. But-1-ene isomerization at different temperatures on zirconium phosphate pretreated in various ways

products...	but-1-ene (%)				isobutene (%)			*cis*-but-2-ene (%)				*trans*-but-2-ene (%)			
pretreatment temperature or zirconium phosphate/°C...	180	300	400	650	300	400	650	180	300	400	650	180	300	400	650
microreactor temperature/°C															
150	99	—	—	91	—	—	—	—	—	—	5	—	—	—	3
200	95	77	50	49	—	—	—	12	13	26	28	9	10	24	23
250	75	51	27	24	—	—	—	15	26	33	34	10	22	40	41
300	65	37	23	22	—	—	—	18	31	34	34	16	32	43.5	44
350	—	29	23	22	—	—	—	—	33	33	33	—	39	44	44
400	—	26	24	24	—	—	—	—	33	32	33	—	41	43	43
450	—	26	26	26	—	0.96	1.3	—	32	32	32	—	42	41	41

bands at 2295 and 2322 cm^{-1} having similar intensities. Such bands correspond to the doublet observed in the liquid at 2254 and 2293 cm^{-1} due to the CN stretching split by Fermi resonance with the $\delta(CH_3)+\nu(CC)$ combination. Such a doublet increases in frequency by coordination on Lewis-acidic cations, as observed in several complexes[24] as well as on Lewis-acidic surfaces.[25] The values we measure on zirconium phosphate confirm the presence of medium-strong Lewis sites.

At higher coverages (fig. 6) another band is evident at 2274 cm^{-1}, while the medium-frequency band is shifted to 2303 cm^{-1}. This illustrates the formation of a second adsorbed species characterized by the doublet at 2274 and 2303 cm^{-1} that is also connected with the formation of a very broad hydrogen-bonded $\nu(OH)$ band. The value of the shift of the $\nu(OH)$ band of hydroxy groups upon interaction with bases may be taken as a measure of the Brönsted strength of such groups. Species characterized by values of the Fermi resonance $\nu(CN)$ doublet very similar to ours are indeed connected to shifts of *ca.* 740 cm^{-1} of the band of the strong Brönsted-acidic hydroxy groups [$\nu(OH) = 3640$ cm^{-1}] of decationized Y-zeolite,[26] of 550 and 230 cm^{-1}, respectively, of the different OH groups of silica–alumina [$\nu(OH) = 3750$ cm^{-1}, unresolved],[27] of *ca.* 300 cm^{-1} of the silanol groups on silica[28] and silicon nitride[29] and of *ca* 200–250 cm^{-1} of the hydroxy groups of alumina.[30] In our case the hydrogen-bonded $\nu(OH)$ band is centred at 3170 cm^{-1} in L-ZrP_2O_7 evacuated at 770 K, while it shifts to 3100 cm^{-1} if evacuation is carried out at 1050 K. Thus the shift increases from 500 to 570 cm^{-1}, indicating that the Brönsted strength is relatively high, and increases further upon dehydration.

No evidence is found for the interaction of hydrogen-bonded OH groups, characterized by the broad $\nu(OH)$ band at 3550–3250 cm^{-1}, with bases from the vapour phase. It thus seems likely that such species are placed in the interlayer region.

Catalytic Tests

The catalytic behaviour of zirconium phosphate in but-1-ene isomerization can be deduced from table 1, which reports the percentages of the different butenes obtained by fluxing but-1-ene into a microreactor (3.3 cm^3 min^{-1}) on 1 g of zirconium phosphate, preheated for 24 h at 453, 573, 673 and 923 K, respectively. The tests refer to different microreactor temperatures and the yields obtained clearly show an increase in but-1-ene conversion on increasing the temperature of thermal preheating.

Since the surface area of the catalyst does not change, the increase in the amount of the reaction products, *cis*- and *trans*-but-2-ene, is indicative of an increase in the strength of the medium-strong Brönsted sites.[31] The detection of small amounts of isobutene, formed by skeletal isomerization, is also indicative of the presence of higher-strength sites.

Conclusions

The catalytic activity of various zirconium phosphate samples, preheated at different temperatures, in but-1-ene isomerization parallels that measured in the dehydration of isopropyl alcohol, as well as that of cation-exchanged zirconium phosphate.[10] It has been ascertained[6, 10] that on zirconium phosphate the catalytically active sites for this type of reaction are only the surface acidic groups, and not those located between the layers, since (*a*) there is a strong decrease in catalytic activity observed on the Cs^+-poisoned samples[6, 10] and (*b*) the transformation of $Zr(HPO_4)_2$ to layered ZrP_2O_7 does not involve any decrease but, on the contrary, an enhancement of the acid-catalysed activity.[10]

With regard to the nature of the acidic sites present on the zirconium phosphate surface, in this work we report clear evidence of the presence either of the expected Brönsted P—O—H sites or of Lewis centres, until now only hypothesized.[6] The presence of the latter can better explain, in the case of alcohol dehydration, the residual catalytic activity observed on the samples poisoned with Cs^+ by ion-exchange of only the surface P—O—H groups. Even if we could verify some degree of crystallite crumbling, consequent to the heating of rehydrated samples, that can make new P—O—H groups available, that had previously been internal, the presence of Lewis sites permits us to explain, especially in the case of L-ZrP_2O_7, the residual activity of the surface Cs-poisoned catalysts. From this we deduce that alcohol dehydration can take place both on the Brönsted and on the Lewis sites of zirconium phosphate phases.

In the case of butene isomerization we must deduce that the reaction can take place only on the Brönsted sites, according to the theory of Hightower and Hall,[32] since null activity has been detected on L-ZrP_2O_7 samples poisoned with Cs^+.[10] The spectroscopic results confirm the medium-strong acidity of zirconium phosphate surfaces, and allow us to propose a model for the corresponding surface sites.

According to the known structure of α-ZrP·H_2O,[15] the exposed (002) layer plane, which is predominant on the surface, is constituted by POH groups that are at a distance of 5.3 Å from each other. This distance is too great to allow hydrogen bonding. Such sites then become free when external-shell water is desorbed, by evacuation at 370 K, and are characterized by the ν(OH) band at 3670 cm^{-1}. Such surface groups would be involved neither in the cavity dehydration occurring below 450 K nor in the condensation of internal POH groups that produces L-ZrP_2O_7. The exposed (002) face is thus expected to be substantially unchanged during thermal dehydration in our temperature range. Such POH groups are also probably predominantly responsible for the development of the surface Brönsted acidity. Their Brönsted strength, according to (i) the slight lowering of the ν(OH) frequency,[33] (ii) the increasing shift upon acetonitrile adsorption, and (iii) the increasing catalytic activity in but-1-ene isomerization, slightly increases upon dehydration and condensation. This may be attributed to a bulk effect arising from the formation of P—O—P bridges in the layered pyrophosphate structure.

Our data indicate that other surface sites, different from such free POH groups, are active, such as Zr^{4+} Lewis-acid sites, ZrOH hydroxy groups and $P(OH)_2$ geminal groups, unexpected on the (002) face. While ZrOH groups probably contribute negligibly to the surface acidity of zirconium phosphate owing to their weak acid strength, geminal $P(OH)_2$ groups may have a role in acid-catalysed reactions. They might be stronger than the single POH Brönsted sites[33] and might be responsible for the formation of small amounts of isobutene from but-1-ene isomerization.

Exposed Zr^{4+} Lewis-acid sites are probably placed on faces perpendicular to the layer planes and may be responsible for the residual activity of Cs-exchanged forms in some acid-catalysed reactions.[10] The detection of ZrOH, Zr^{4+} and $P(OH)_2$ exposed sites suggest the relevance of perpendicular faces or surface defects in the surface chemistry of zirconium phosphate.

The technical collaboration of Dr G. Oliveri in the word-processing preparation of the manuscript is gratefully acknowledged.

References

1 A. Clearfield, in *Inorganic Ion-exchange Materials*, ed. A. Clearfield (CRC Press, Boca Raton, Fla, 1982), p. 1.
2 S. E. Horsley and D. V. Nowell, *Thermal Analysis*: *Proc. Third ICTA*, Davos (1971), vol. 2, p. 611.
3 A. La Ginestra, M. A. Massucci, C. Ferragina and N. Tomassini, *Proc. Fourth ICTA*, Budapest (1974), vol. 1, p. 631.
4 U. Costantino and A. La Ginestra, *Thermochim. Acta*, 1982, **58**, 179.
5 A. La Ginestra, C. Ferragina, M. A. Massucci, P. Patrono, R. Di Rocco and A. A. G. Tomlinson, *Gazz. Chim. Ital.*, 1983, **113**, 357.
6 A. Clearfield and D. S. Thakur, *J. Catal.*, 1980, **65**, 185.

7 A. Clearfield, *J. Mol. Catal.*, 1984, **27**, 235.
8 K. Segawa, Y. Kurusu, Y. Nakajima and M. Kinoshita, *J. Catal.*, 1985, **94**, 491.
9 T. Hattori, A. Ishiguro and Y. Murakami, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1107.
10 A. La Ginestra, P. Patrono, M. L. Berardelli, P. Galli, G. Farragina and M. A. Massucci, *J. Catal.*, in press.
11 A. Clearfield and J. Stynes, *J. Inorg. Nucl. Chem.*, 1974, **26**, 117.
12 S. E. Horsley, D. V. Nowell and D. T. Stewart, *Spectrochim. Acta, Part A*, 1974, **30**, 535.
13 L. W. Schroeder, T. W. Jordan and W. E. Browen, *Spectrochim. Acta, Part A*, 1981, **37**, 21.
14 B. Marchov and A. Novak, *J. Chem. Phys.*, 1983, **78**, 2105.
15 J. M. Troup and A. Clearfield, *Inorg. Chem.*, 1977, **16**, 3311.
16 G. Busca, F. Cavani, G. Centi and F. Trifirò, *J. Catal.*, 1986, **99**, 400.
17 Y. Inomata, T. Inomata and T. Moriwaki, *Spectrochim. Acta, Part A*, 1986, **36**, 839.
18 G. Busca and J. C. Lavalley, *Spectrochim. Acta, Part A*, 1986, **42**, 443.
19 J. B. Peri, *Discuss. Faraday Soc.*, 1971, **52**, 55.
20 J. Haber and V. Szybalska, *Discuss. Faraday Soc.*, 1981, **72**, 263.
21 G. Busca, G. Centi, F. Trifirò and V. Lorenzelli, *J. Phys. Chem.*, 1986, **90**, 1337.
22 T. Yamaguchi, Y. Nakano and K. Tanabe, *Bull. Chem. Soc. Jpn*, 1978, **51**, 2482.
23 Y. Nakano, T. Iizuka, H. Hattori and K. Tanabe, *J. Catal.*, 1979, **57**, 1.
24 J. Reedijk, A. P. Zuur and W. L. Groeneveld, *Recl. Trav. Chim.*, 1967, **86**, 1127.
25 G. Busca, G. Centi and F. Trifirò, *J. Am. Chem. Soc.*, 1985, **107**, 7757.
26 C. L. Angell and M. V. Howell, *J. Phys. Chem.*, 1969, **73**, 2551.
27 R. E. Sempels and P. G. Rouxhet, *J. Colloid Interface Sci.*, 1976, **55**, 263.
28 D. Kunath and D. Shulz, *J. Colloid Interface Sci.*, 1978, **66**, 379.
29 G. Busca, V. Lorenzelli, G. Porcile, M. I. Baraton, P. Quintard and R. Marchand, *Mater. Chem. Phys.*, 1986, **14**, 123.
30 H. Krietenbrink and H. Knözinger, *Z. Phys. Chem. N.F.*, 1976, **102**, 43.
31 J. P. Damon, B. Delmon and J. M. Monnier, *J. Chem. Soc., Faraday Trans. 1*, 1977, **73**, 372.
32 J. W. Hightower and W. K. Hall, *J. Phys. Chem.*, 1967, **71**, 104.
33 P. A. Jacobs, W. J. Mortier and J. B. Uytterhoeven, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1919.

Paper 6/816; *Received* 28*th April*, 1986