Surface Acidity of the Layered Pyrophosphates of Quadrivalent Ti, Zr, Ge, and Sn and Their Activity in Some Acid-catalysed Reactions

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The layered pyrophosphates of quadrivalent Ti, Zr, Ge, and Sn have been prepared and characterized by Fourier-transform i.r. spectroscopy, differential thermal analysis, thermogravimetry, *X*-ray diffraction, and surface area measurements. Their surface acidity has been investigated by Fourier-transform i.r. spectroscopy, with an analysis of the OH stretching region and of the spectra of adsorbed basic molecules (pyridine and acetonitrile), as well as by measuring their activity in acid-catalyzed reactions. The trend of the surface Bronsted-acid strengths found was Ge $>$ Sn $\gg$ Ti $>$ Zr, corresponding to the trend in electronegativity of the elements, while the opposite trend was found for the surface Lewis-acid strengths.

The layered phosphates of Zr and Ti have been shown to be active as ion exchangers[1,2] and as catalysts in typical acid-catalyzed reactions such as alcohol dehydration,[3,4] olefin isomerization,[4,5] as well as hydrocarbon synthesis from methanol.[6] In the case of the zirconium compounds it has been shown that the surface Bronsted acidity slightly increases during thermal treatment, dehydration of the starting bis(hydrogenphosphate) monohydrate resulting in the anhydrous hydrogenphosphate and, at higher temperatures (873—973 K), the layered pyrophosphate.[7] Cubic pyrophosphates are formed only above 1 173 K. The corresponding compounds of germanium[8] and tin[9] have also been studied from the point of view of their solid-state chemistry, in the same range of temperatures they give compounds similar to those found for Zr and Ti.

The present paper deals with the characterization of the layered pyrophosphates of Ti, Zr, Ge, and Sn and of their surface acid strength, determined using i.r. spectroscopy and catalytic tests. The aim was to try to obtain a correlation of the Lewis and Bronsted acid strengths with the quadrivalent element.

Experimental

The layered pyrophosphates of Zr, Ti, Sn, and Ge were prepared by thermal dehydration of the corresponding bis(hydrogenphosphate) monohydrates, prepared as reported elsewhere,[8–11] by heating for 12 h at 773 K (in the cases of Ge, Sn, and Ti) or at 923 K (in the case of Zr). The thermal gravimetry (t.g.), differential thermal analyses (d.t.a.), and *X*-ray diffraction (Philips diffractometer, Cu-K_α radiation) apparatus has been described elsewhere.[8,10]

Fourier-transform i.r. spectra were recorded using a Nicolet MX1 spectrometer. Adsorption experiments were performed using pressed disks of the pure powders, which were activated *in vacuo* in an i.r. cell. The catalytic tests were performed in a quartz flow-microreactor fed with 1-butene. The products were collected and analyzed using a Carlo Erba model 4300 gas chromatograph. Chromosorb W–10% squalane columns were used for the separations.

Results

(*a*) *Structural and Surface Area Characterizations.*—Evidence of the existence of the layered pyrophosphates of Zr and Ti was given previously by Costantino and La Ginestra,[11] on the basis of *X*-ray diffraction and density measurements and structural considerations. The four pyrophosphates are formed upon heat treatment of the corresponding hydrogenphosphates at temperatures between 570 and 920 K, after an endothermic peak in the d.t.a. curves and a weight loss corresponding to one water molecule per metal atom in the t.g. curves. The *X*-ray powder diffraction spectra are summarized in Table 1. Given the maintenance of the layered structure,[11] the first reflection corresponds to the interlayer distance.

The Fourier-transform i.r. spectra of the four layered pyrophosphates in the skeletal (1 400—400 cm^{-1}) region are reported in Figure 1. They are different from those of the more stable cubic forms[12,13] confirming that we are dealing with another crystal phase. In all cases a broad absorption containing the poorly resolved $\nu_{asym}(PO_3)$ and $\nu_{sym}(PO_3)$ modes is observed in the region 1 000—1 300 cm^{-1} and several PO_3 deformations in the region below 650 cm^{-1}. The more typical modes characterizing the pyrophosphate compounds are those due to the vibration of the P–O–P bridge; its symmetric stretching is observed at 725 cm^{-1} for the tin compound, split at 745 and 760 cm^{-1} for the titanium compound, and at 760 and 790 cm^{-1} respectively for the layered pyrophosphates of Zr and Ge. The corresponding asymmetric stretching is well resolved in the cases of Ge (990 cm^{-1}) and Ti (980 and 958 cm^{-1}), while it is

Table 1. *X*-Ray powder-diffraction spectra of the layered pyrophosphates

L-SnP_2O_7		L-GeP_2O_7		L-TiP_2O_7		L-ZrP_2O_7	
d/Å	Intensity	*d*/Å	Intensity	*d*/Å	Intensity	*d*/Å	Intensity
6.25	m	6.14	s	6.94	s	6.10	s
4.29	ms	3.78	ms	4.24	ms	5.12	mw
4.09	ms	3.03	vw	3.90	m	4.31	w
3.55	ms	2.73	mw	3.35	vw	4.12	ms
2.49	s	2.39	ms	2.50	mw	3.69	w
2.31	w					3.50	w
						3.05	vw
						2.92	vw
						2.64	m

s = Strong, m = medium, and w = weak.

present as a shoulder (near 960 and 930 cm^{-1}) for Zr and Sn. In the case of L-TiP_2O_7 it is split, probably indicating the presence of two different types of pyrophosphate groups. Both stretching frequencies shift in the same way in the four compounds.

It is difficult at this time to find correlations between the interlayer distances, deduced by *X*-ray diffraction, and the ionic radii or the strength of the P–O–P bonds deduced from the values of the P–O–P stretching frequencies, since the crystal structure of the layered pyrophosphate has not been resolved.

The determination of the surface areas, performed by the Brunauer, Emmet, and Teller method, gave the following results: L-GeP_2O_7, 8.8; L-SnP_2O_7, 3.5 L-TiP_2O_7, 7.0; and L-ZrP_2O_7, 4.2 m^2 g^{-1}.

(*b*) *Infrared Characterization of the Surface* OH *Groups*.—The Fourier-transform i.r. spectra of the four layered pyrophosphates (pressed disks of the pure powders) in the 4 000—3 500 cm^{-1} region after surface dehydration by heating *in vacuo* are reported in Figure 2. In all four cases a sharp ν(OH) band centred between 3 665 and 3 650 cm^{-1} is predominant and looks similar to the bands detected under similar conditions for samples of other phosphate compounds such as $AlPO_4$,[14] BPO_4,[15] $(VO)_2P_2O_7$[16] as well as phosphorus-treated silica.[17,18] In all such cases this sharp band is surface-sensitive, being perturbed upon adsorption, and has been assigned to the OH stretching of free surface POH groups. A band very similar to that predominant for the layered pyrophosphates although at a slightly higher frequency is also observed for samples evacuated at a lower temperature (Figure 3) that are structurally hydrogenphosphates, bulk decomposition still being negligible. Accordingly, these samples also show a very strong absorption in the region 3 500—2 800 cm^{-1} due to bulk POH groups (Figure 3). As discussed previously in the case of the zirconium compounds,[7] both the cavity dehydration of the starting bis(hydrogenphosphate) monohydrates and the bulk dehydration of the anhydrous hydrogenphosphates are expected to leave substantially unchanged the predominantly exposed 'layer' ⟨002⟩ face of the starting compound, where hydrogenphosphate ions cannot condense, due to the absence of an available 'partner' at an appropriate distance. We assign then the band at 3 660—3 650 cm^{-1} in all four cases to ν(OH) of free POH groups of the hydrogenphosphate ions on the 'layer' face of the pyrophosphate compounds, at a distance similar to that of the starting bis(hydrogenphosphate) hydrate. Such a distance (5.3 Å in the zirconium compound[19]) is too large to allow hydrogen bonding between the nearest POH groups, in agreement with the sharpness of the ν(OH) band and its high wavenumber.

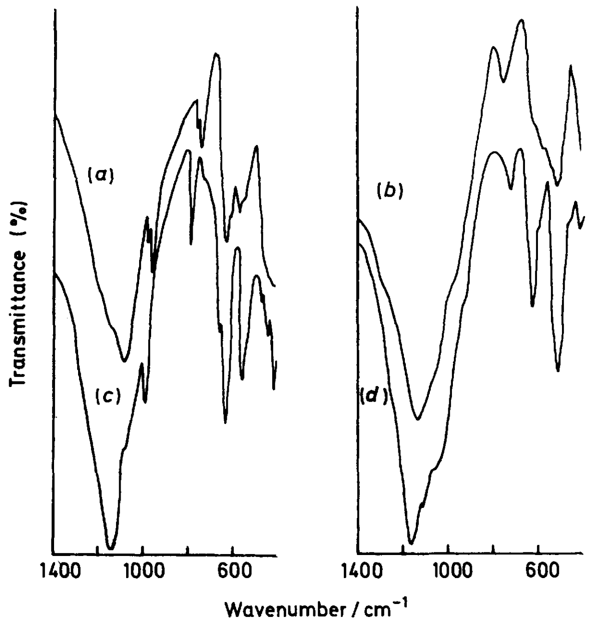

Figure 1. Fourier-transform i.r. spectra (KBr pressed disks) of L-TiP_2O_7 (*a*), L-ZrP_2O_7 (*b*), L-GeP_2O_7 (*c*), and L-SnP_2O_7 (*d*)

Besides this predominant band, other weaker ν(OH) bands are observable in the spectra of the pyrophosphate samples (Figure 2). In the case of GeP_2O_7 another slightly broader maximum is detectable near 3 620 cm^{-1}, while for ZrP_2O_7 a similar band is observable with more difficulty near 3 600 cm^{-1}. In the cases of TiP_2O_7 and SnP_2O_7 the main ν(OH) band is asymmetric towards lower frequencies, although a maximum is not resolved. A broader and weaker maximum at lower frequency with respect to the POH band discussed above has frequently been detected for phosphate catalysts[15–17] and assigned to ν(OH) of geminal $P(OH)_2$ groups. Rather weak

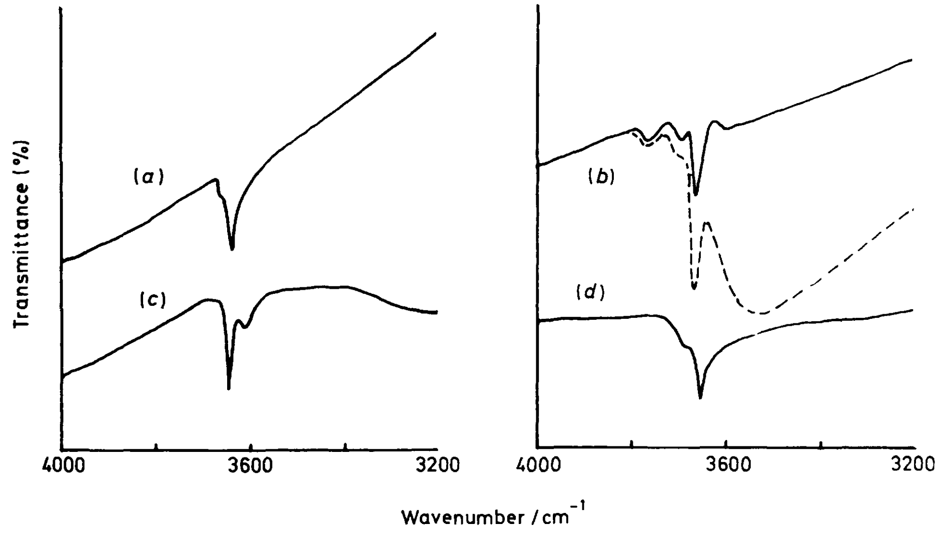

Figure 2. Fourier-transform i.r. spectra of pressed disks of pure L-TiP_2O_7 activated at 923 K (*a*), L-ZrP_2O_7 activated at 900 [(*b*) broken line] and 1 050 K [(*b*), full line], of L-GeP_2O_7 activated at 1 073 K (*c*), and of L-SnP_2O_7 activated at 973 K (*d*)

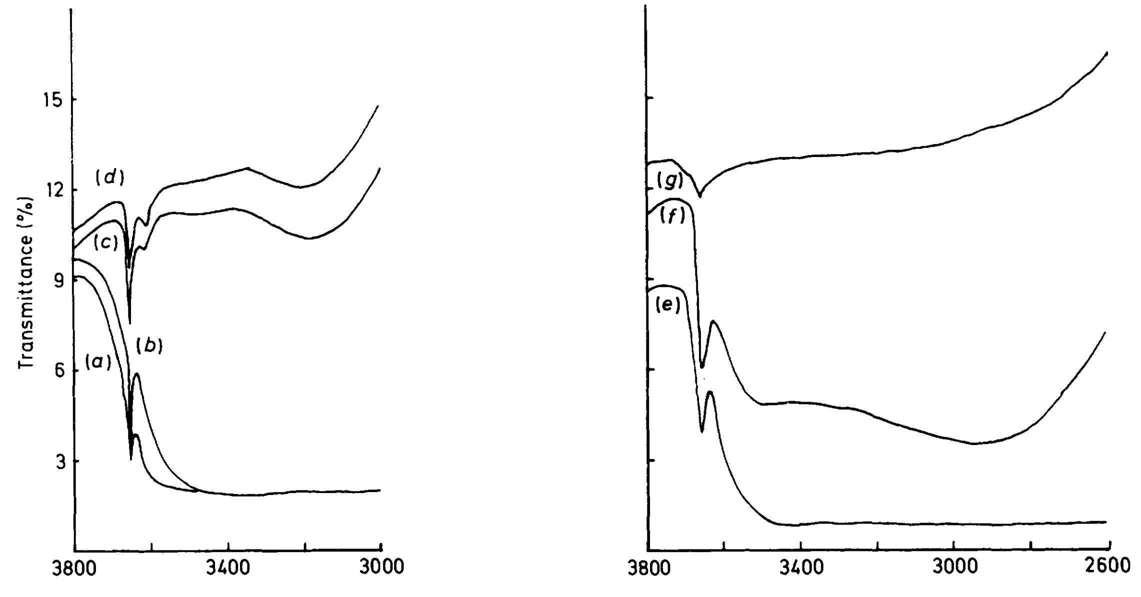

Figure 3. Fourier-transform i.r. spectra of an α-Ge(HPO$_4$)$_2$·H$_2$O pressed disk after heat treatment *in vacuo* at 573 (*a*), 673 (*b*), 773 (*c*), and 1 073 K (*d*), and of α-Sn(HPO$_4$)$_2$·H$_2$O after heat treatment at 573 (*e*), 773 (*f*), and 973 K (*g*)

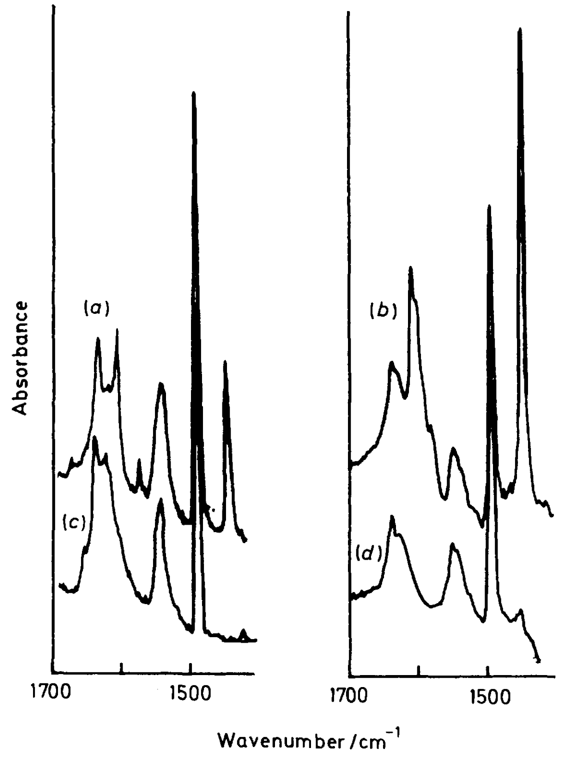

Figure 4. Fourier-transform i.r. spectra of pyridine adsorbed on L-TiP$_2$O$_7$ (*a*), L-ZrP$_2$O$_7$ (*b*), L-GeP$_2$O$_7$ (*c*), and L-SnP$_2$O$_7$ (*d*)

maxima are also observable at higher frequencies with respect to the main band, namely at 3 770, 3 700 cm^{-1} for ZrP$_2$O$_7$, at 3 705 cm^{-1} for SnP$_2$O$_7$, and at 3 680 cm^{-1} for TiP$_2$O$_7$. Such bands, by comparison with the spectra of the surface hydroxy groups of the corresponding oxides ZrO$_2$,[20] SnO$_2$,[21] and TiO$_2$,[22] may tentatively be assigned to ν(OH) of MOH groups (M = Zr, Sn, or Ti). Such groups, that are not expected on the 'layer' plane of the pyrophosphate structure, where all co-ordinative valences of the octahedral cations are saturated by the phosphate ligand, may instead be present on planes perpendicular to the layers, where such OH groups may be needed to saturate the co-ordination sphere of exposed cations or in surface defects. It may be of interest that GeOH groups, if any, are expected to exhibit a frequency (near 3 670 cm^{-1} for GeO$_2$[23] and Ge-treated silica[18]) very similar to that of the free POH groups, and might then be masked in the spectrum of the germanium pyrophosphate.

Literature data indicate that while phosphate catalysts are generally strong Bronsted acids,[14–16] the oxides of Zr, Ti, and Sn are not;[20–22] GeOH groups are also believed to be much less acidic than POH groups.[18] It seems then to be a reasonable approximation to assume that the most important surface Bronsted acidity of the layered pyrophosphates is prevalently due to the surface POH and/or P(OH)$_2$ groups, although other hydroxy groups are also present in smaller amounts.

(*c*) *Adsorption of Pyridine.*—Pyridine represents a very useful probe molecule for the characterization of surface acidity.[24] The adsorption of pyridine on all four pyrophosphates (Figure 4) produces bands near 1 640 and 1 545 cm^{-1}, typical of pyridinium cation. So, the presence of Bronsted acid sites is confirmed. However, bands typical of pyridine chemisorbed as such on Lewis-acid sites (in particular the 8a mode at 1 600—1 610 cm^{-1} and the 19b mode near 1 445 cm^{-1}) are observed only in the cases of Zr and Ti. In the cases of Ge and Sn, after evacuation at room temperature, such bands are absent indicating that pyridine does not adsorb irreversibly on the surface of these pyrophosphates.

(*d*) *Adsorption of Acetonitrile.*—Acetonitrile has been shown to be a more useful probe molecule even than pyridine for the i.r. evaluation of the strength of both Lewis and Bronsted surface acid sites.[7,25] When acetonitrile vapour is admitted into an i.r. cell containing the activated pyrophosphate samples, a couple

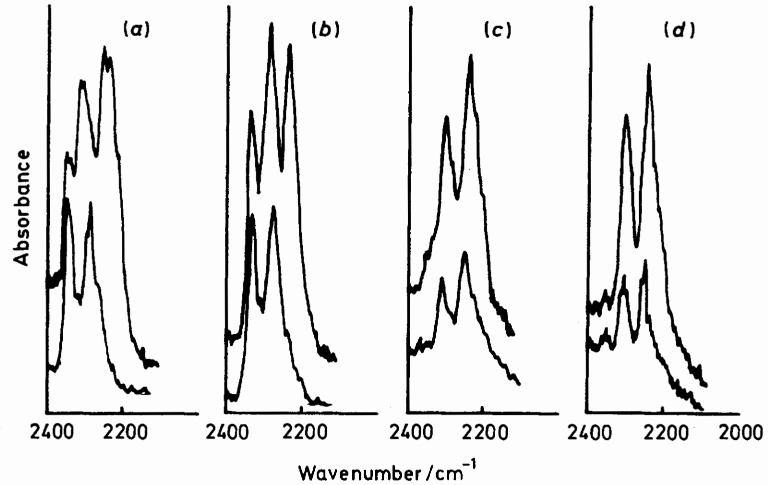

Figure 5. Fourier-transform i.r. spectra of acetonitrile adsorbed on L-TiP_2O_7 (*a*), L-ZrP_2O_7 (*b*), L-GeP_2O_7 (*c*), and L-SnP_2O_7 (*d*). Upper curves, acetonitrile pressure *ca.* 3 Torr (400 Pa); lower curves, very low acetonitrile pressure

of bands appear in the region 2 350—2 250 cm^{-1}, due to splitting of the ν(CN) fundamental (ν_2) of the adsorbed acetonitrile by Fermi resonance with a ν(CC) + δ(CH_3) ($\nu_4 + \nu_3$) combination.[26,27] Both the frequencies and relative intensities of such bands are sensitive to the strength of the absorption bond: by increasing the electron-withdrawing strength of the adsorption site, the unperturbed value of the ν(CN) fundamental wavenumber increases and falls nearer and even overtakes the unperturbed value of the combination, which also slightly increases due to the increase in the ν_4 [ν(CC)] fundamental.[26,27]

When small amounts of the adsorbate are admitted, the ν(OH) bands discussed above are not perturbed, indicating that adsorption does not take place on hydroxyls. The wavenumbers of the ν(CN) Fermi-resonance doublet observed for acetonitrile adsorbed on the four pyrophosphates (Figure 5) are compared in Table 2 with those observed for other catalysts, as well as for the liquid molecule. For the pyrophosphates of Zr and Ti the two components have almost similar intensities and fall at relevantly high wavenumbers, while in the cases of Ge and Sn the lower-frequency component is much more intense, and both fall at only slightly higher frequencies with respect to the liquid. In the case of the titanium compound, the observed frequencies may be compared with those observed for acetonitrile adsorbed on the corresponding oxide TiO_2 (anatase 2 310, 2 280 cm^{-1} [28]), as well as for the complex $TiCl_4$·2 CH_3CN (2 315, 2 310; 2 288, 2 283 cm^{-1} [29]). The similarity of the observed frequencies supports the assignment of the bands to acetonitrile chemisorbed on co-ordinatively unsaturated Ti^{4+} cations. In good agreement with the results observed using pyridine as a probe molecule, then, adsorbed acetonitrile confirms the presence of relatively strong Lewis-acid centres on both the pyrophosphates of Ti and Zr, while on the pyrophosphates of Ge and Sn they are, if any, much weaker. As discussed previously for layered zirconium phosphates,[7] co-ordinatively unsaturated cations are not expected on the 'layer' planes, arising from the ⟨002⟩ plane of the starting α-$M(HPO_4)_2$·H_2O compound, but may be present in perpendicular planes.

When higher amounts of acetonitrile vapour are admitted to the i.r. cell the ν(OH) bands discussed above begin to disappear, being substituted by very broad absorptions centred at much lower frequencies. Such broad absorptions are attributed to ν(OH) of the predominant POH groups when they are hydrogen-bonded to acetonitrile. Correspondingly, in the ν(CN) region a doublet grows at wavenumbers similar to those of other hydrogen-bonded species,[25,29] near 2 300 and 2 270 cm^{-1}. In the cases of Ti and Zr, such new bands are clearly resolved from those of the more strongly perturbed chemisorbed acetonitrile species, discussed above. It has been reported that the shift of the ν(OH) band when an hydroxy group is involved in hydrogen bonding may be taken as a measure of the acid strength of the OH group.[30] Such a so-called hydrogen-bonding method has been applied to evaluate the acid strength of the hydroxy groups on solid surfaces.[31,32] In Table 2, the shifts undergone by ν(OH) of the hydroxy groups of some solid catalyst surfaces upon acetonitrile adsorption are compared and evidence the strong Bronsted surface acidity of the layered pyrophosphates.

Table 2. Observed wavenumbers (cm^{-1}) for acetonitrile adsorbed on solid surfaces and ν(OH) shifts for surface hydroxy groups

Chemisorbed species			Hydrogen-bonded species			
Surface	ν(CN)[a]	Ref.	Surface	ν(OH)	Δν(OH)	Ref.
BPO_4	2 337, 2 315	*b*	HY-zeolite	3 640	740, 1 200	*c*
Al_2O_3	2 328, 2 300	26	GeP_2O_7	3 657	750	*d*
$(VO)_2P_2O_7$	2 328, 2 300	25	SnP_2O_7	3 660	690	*d*
ZrP_2O_7	2 322, 2 295	*d*	TiP_2O_7	3 653	580	*d*
TiP_2O_7	2 320, 2 290	*d*	ZrP_2O_7	3 664	560	*d*
TiO_2	2 310, 2 280	28	SiO_2–Al_2O_3	3 750	550	*e*
SnP_2O_7	2 310, 2 279	*d*	SiO_2	3 745	300	*e*
GeP_2O_7	2 307, 2 276	*d*	Al_2O_3		$\leqslant$250	
Liquid	2 293, 2 254	26				

[a] Split due to Fermi resonance (see text). [b] L. E. Kitaev, A. A. Kubasov, and K. V. Topchieva, *Kinet. Katal.*, 1976, **17**, 780. [c] C. L. Angell and M. V. Howell, *J. Phys. Chem.*, 1969, **73**, 2551. [d] This work. [e] R. E. Sempels and P. G. Rouxhet, *J. Colloid Interface Sci.*,1976, **55**, 263.

(*e*) *Activity in Acid-catalyzed Reactions.*—The catalytic activity of the zirconium layered pyrophosphate in some acid-catalyzed reactions, such as alcohol dehydration and butene isomerization, has been reported previously[4,7,10] and was shown to be higher than those of the corresponding cubic pyrophosphate and of the various hydrogenphosphates pretreated at different temperatures. A detailed study of the

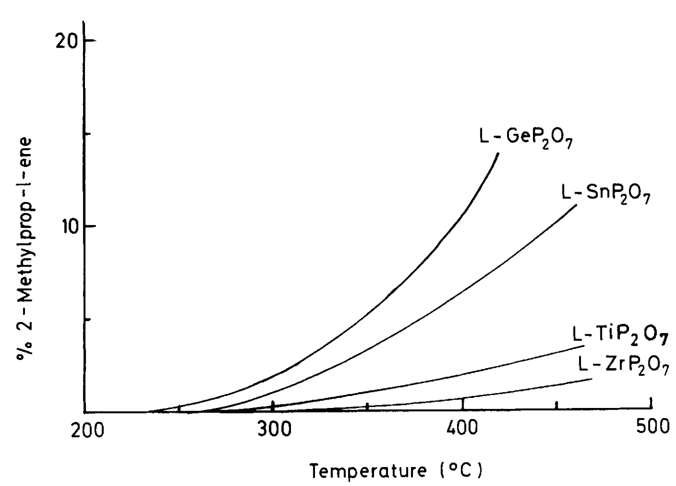

Figure 6. Yields of 2-methylprop-1-ene in the 1-butene isomerization as a function of the reaction temperature on the layered pyrophosphate catalysts

Table 3. Products of 1-butene isomerization at 703 K on different layered pyrophosphate phases

		Product (%)			
Catalyst	Time/h	1-Butene	2-Methylprop-1-ene	*trans*-2-Butene	*cis*-2-Butene
α-L-ZrP_2O_7	1	27.0	1.4	41.0	39.5
(*a*)	2	28.0	1.0	40.0	31.0
α-L-TiP_2O_7	1	25.0	1.8	42.0	31.0
(*b*)	1.5	27.0	1.0	40.0	30.0
	2.5	33.0	0.5	37.0	29.0
α-L-GeP_2O_7	1	19.7	20.6	33.5	24.4
(*c*)	2	21.0	16.8	35.6	25.7
	3	21.7	14.5	36.5	26.5
α-L-SnP_2O_7	1	20.3	18.6	34.7	24.8
(*c*)	2	21.8	13.0	37.4	27.1
	3	23.0	8.8	39.2	28.4
	4	23.5	6.1	40.7	29.3

Pretreatment at (*a*) 873, (*b*) 723, or (*c*) 773 K.

catalytic activity of the different phases derived by heating the hydrogenphosphates of Ti, Ge, and Sn will be reported elsewhere.[33] Some results concerning L-$M^{IV}P_2O_7$ (M = Zr, Ti, Ge, or Sn) are reported here to verify the above spectroscopic data on a reactivity basis.

It is well known[34] that the 1-butene isomerization can be used as a good test to obtain information on the strength of the acidic sites present on a catalyst, since weak Bronsted sites can give only some configuration isomerization, medium strong sites can give rise to double-bond isomerization, and only strong sites result in skeletal isomerization with the formation of 2-methylprop-1-ene. Therefore the higher the yields of the latter, under the same (T and τ) conditions (τ = contact time) the stronger is the strength of the Bronsted sites on the catalyst.

In Table 3 are reported the results obtained by fluxing in a microreactor charged with 0.5 g of catalyst a flow of 1-butene of 1.5 cm^3 min^{-1} (τ = 2.4 g catalyst per g 1-butene per h). The various compounds were first treated at the temperatures necessary to obtain the corresponding layered pyrophosphate phase. All the tests were performed at 703 K. The product sum sometimes differs slightly from 100% because of the simultaneous formation of small amounts of cracking products of other C_4 hydrocarbons. From these data it can be inferred that (a) the catalytic activity (conversion of 1-butene) of the four L-pyrophosphates in the 1-butene isomerization at 703 K decreases in the order Ge > Sn $\gg$ Ti > Zr, and therefore, given that their surface areas are small and comparable, this sequence must be ascribed mainly to the different strengths of the surface Bronsted sites, which evidently decreases in the same order; (b) this trend is confirmed by the decrease in yields of 2-methylprop-1-ene obtained in the order Ge > Sn $\gg$ Ti > Zr.

By increasing the working time a decrease in the 2-methylprop-1-ene yields has been recorded for all samples, as well as a partial deactivation of all catalysts: both effects can be related to the observed formation of black deposits on the particles, evidently due to some concomitant coking reactions occurring for this class of compounds.

By increasing the temperature of the tests an increase in the yields of 2-methylprop-1-ene is observed in all cases, as shown in Figure 6. Furthermore, in the temperature range investigated (473—723 K) the ability to give rise to skeletal isomerization always follows the same order, Ge > Sn $\gg$ Ti > Zr, thus confirming that the strength of the surface P–O–H groups in the four L-pyrophosphates retains the same order upon varying the reaction temperature.

Discussion

The thermal treatment of the compounds α-$M(HPO_4)_2 \cdot H_2O$ (M = Zr, Ti, Sn, and Ge) produces analogous compounds that have been identified as layered pyrophosphates. These compounds exhibit an acid-type catalytic activity, which varies slightly depending on the element. The i.r. study of pressed disks of the pure compounds has shown that surface hydroxy groups are present. The predominant surface groups are responsible for characteristic ν(OH) bands near 3 650 cm^{-1} and are identified as POH groups from hydrogenphosphate ions on the 'layer' face of the pyrophosphate structure, although evidence was also found for the presence of $P(OH)_2$ geminal groups and of MOH (M = Zr, Ti, Sn, and Ge) hydroxy groups, probably in smaller amounts.

The surfaces of the four layered pyrophosphates show a Bronsted acidity, revealed by the protonation of pyridine in the form of the adsorbed pyridinium cations as well as by a catalytic activity towards 1-butene isomerization. The adsorption of acetonitrile at high coverages allows us to evaluate the relative strengths of such predominant POH groups, through the shift of the ν(OH) band upon hydrogen bonding. The strength of the predominant surface Bronsted sites of the pyrophosphate compounds, thus evaluated, is very high, in the cases of Ge and Sn being higher than that of silica–alumina, for example. It decreases in the order Ge $\geqslant$ Sn > Ti > Zr, in accord with the catalytic activity towards 1-butene isomerization. It is of interest that the same trend has also been observed for the vibrational perturbation undergone by the cavity water molecule in the corresponding four bis(hydrogenphosphate) hydrates,[35] following hydrogen bonding of different strengths with the structural hydrogenphosphate ions.

The spectroscopic study of the adsorption of the basic probe molecules pyridine and acetonitrile indicates that Lewis-acid sites exist on the surface of the pyrophosphates of Ti and Zr, while such sites are weaker by far, if they exist, in the cases of Ge and Sn. In particular, the bands of the ν(CN) Fermi-resonance doublet indicate the following trend for the Lewis-acid strength on the layered pyrophosphates: Zr $\geqslant$ Ti $\gg$ Sn $\approx$ Ge.

Since the four compounds are believed to be structurally similar, being derived from isostructural hydrogenphosphates and all giving isostructural α-cubic pyrophosphates, it seems reasonable to try to correlate the above trends evidenced for the surface Bronsted- and Lewis-acid strengths to some character of the quadrivalent six-co-ordinated cations. Accordingly, a correlation may be proposed with the electronegativity of the elements, which decreases in all proposed scales in the order Ge > Sn $\gg$ Ti > Zr,[36] and corresponds to the order of the acid strength found from the catalytic tests. It then seems reasonable to propose that the Bronsted-acid strength of the surface POH groups increases with increasing covalency of the (PO)–M bond, which may cause an increase in the ionic character of the POH bonds. However, increased covalency of the metal–phosphate bonds decreases the cationic character of the bonded metal atoms, so decreasing their Lewis-acid strength when they are exposed on the external crystal surface.

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