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Catalytic Activity of Zirconium Phosphate and Some Derived Phases in the Dehydration of Alcohols and Isomerization of Butenes

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The catalytic activity of α-$Zr(HPO_4)_2 \cdot H_2O$ prepared by different methods and of phases derived from it by heating between 200 and 1100°C or by ion exchange with Na^+, Cs^+, or Ag^+, has been investigated by means of different acid-catalyzed test reactions, namely, isopropanol, 1- or 2-butanol dehydration, and 1-butene isomerization. The active centers of both $Zr(HPO_4)_2$ and ZrP_2O_7 phases are mainly the surface Brønsted sites, as indicated by the strong decrease or annihilation of their catalytic activity after surface Cs^+ poisoning. An explanation of the low residual activity detected for some samples is given. As deduced from the products of 1-butene isomerization, the acidic sites are generally of medium strength. However, on heating between 350 and 700°C, when partial or total condensation of hydrogen phosphate to P–O–P groups occurs (with progressive formation of the layered pyrophosphate phase) they transform into sites of medium-high strength.

INTRODUCTION

Over the last few years, inorganic ion exchangers belonging to the class of layered acid phosphates or arsenates of tetravalent metals (with the formula $M(IV)HXO_4)_2 \cdot H_2O$ (M = Ti, Zr, Sn, Ge; X = P, As) have received increasing attention because they are able to promote several acid-catalyzed reactions. Furthermore, these materials, when thermally treated, pillared with organic guests, or exchanged with transition metal ions are now widely investigated for various promising applications. The most important catalytic properties have been recently reviewed (*1–4*).

A particularly crucial point to clarify is the understanding of the factors on which the strength of the acidic centers present depends. This presupposes investigating how their catalytic properties are modified by (i) changing the conditions of preparation, (ii) the type of thermal pretreatment, (iii) the presence of other ions, introduced by ion exchange, etc.

We have undertaken a systematic study of the influence of the different tetravalent metals (Ti, Zr, Sn, Ge) or pentavalent elements (P, As) on the strength of acidic centers in such isostructural materials (*5*).

We report here the data obtained with α-zirconium phosphate, prepared by two different methods, and with the derived phases obtained either by thermal treatment or ion exchange. As catalytic test reactions we have chosen the dehydration of isopropanol and 1- and 2-butanol, and the isomerization of 1-butene. The last mentioned reaction is useful because the products obtained can provide information on the strength of the acidic centers present (*6*).

These basic data are necessary for a wider comparison with the properties of the other phosphates or arsenates of tetravalent metals, either in pure or in mixed phases.

EXPERIMENTAL

Chemicals. All the reagents were Carlo Erba RP ACS, except $ZrOCl_2 \cdot 8H_2O$, which was a Merck "pro analysi" product.

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Materials. Crystalline α-zirconium acid phosphate, α-$Zr(HPO_4)_2 \cdot H_2O$, was prepared either by refluxing the amorphous product[1] in 10 mol dm^{-3} H_3PO_4 for 100 h ($ZPH_2 \cdot H_2O$ 10/100) (*7*), or by direct precipitation (dp) from a solution 0.13 mol dm^{-3} in $ZrOCl_2 \cdot 8H_2O$, 1.12 mol dm^{-3} in HF, and 5.1 mol dm^{-3} in H_3PO_4, warmed on a water bath at about 80°C in order to accelerate the precipitation by decomplexing the zirconium fluorocomplex (*8*) ($ZPH_2 \cdot H_2O$ dp). The latter possesses a higher degree of crystallinity than the former. To obtain complete dehydration, both materials were heated at 180°C for 12 h (*4*); they were then treated at the desired temperatures in an O_2 flow for 12 h before use as catalysts. Layered zirconium pyrophosphate (L-Py) was obtained by heating ZPH_2 10/100 or dp at 600 or 700°C for 12 h (*9*). Cubic zirconium pyrophosphate (α-Py) was prepared by heating ZPH_2 10/100 at 1000°C or ZPH_2 dp at 1200°C (*9*).

Sodium or silver zirconium phosphate materials were prepared by ion exchange according to known methods (*10, 11*). The phases chosen were $ZrHNa(PO_4)_2$, $Zr(NaPO_4)_2$, and $ZrH_{1.6}Ag_{0.4}(PO_4)_2$; all were obtained from the corresponding hydrated forms heated at 300°C for 12 h in O_2 flow before use in the catalytic tests.

Physicochemical measurements. The thermal behavior of the different materials was followed with a Stanton Model 801 simultaneous DTA-TG-DTG thermoanalyzer (Pt crucibles, Pt–Pt/Rh thermocouples, heating rate 2–5°C/min). The structural modifications caused by the thermal treatments were checked by taking the X-ray powder patterns on a Philips diffractometer (Ni-filtered Cu$K\alpha$ radiation).

The surface area measurements of the samples were performed by the BET method by measuring the N_2 adsorbed at −180°C. In some cases the surface area was also calculated from the lowering of pH consequent on the contact of a known amount of ZPH_2 10/100 or dp with a defined volume of 0.1 mol dm^{-3} $CsNO_3$ solution. Cs^+ ions exchange only the protons of the surface (*12*). The procedure was repeated with fresh Cs^+ solution until the decrease in pH was no longer observed.

The catalytic tests were performed in a quartz flow microreactor fed with 1-butene or He saturated with iso-C_3 or C_4 alcohols.

A known amount of catalyst (1–3 g) was accurately weighed and loaded into the reactor. It was heated overnight at the desired temperatures in O_2 flow prior to starting the catalytic runs. The products were collected and analyzed by using a Carlo Erba Model 4300 gas chromatograph. Poropak Q 80/100 (alcohol dehydration) or Chromosorb W–squalane 10% (butene isomerization) columns were used for the separations.

All the zirconium phosphate phases employed in the catalytic tests are reported in Table 1, with their chemical formulas corresponding to the temperatures at which they were treated, interlayer distances and surface areas measured by the BET method or by the Cs^+/H^+ ion-exchange procedure.

RESULTS

Before discussing the results of the catalytic tests, some comments are in order on the thermal behavior of α-$Zr(HPO_4)_2 \cdot H_2O$.

Several authors have prepared this compound and studied its thermal behavior (*9, 13–16*). A comparison of the results has demonstrated that the shape of the TG-DTA-DTG curves and the crystalline phases obtained at fixed temperatures depend on the preparation method used for obtaining the material and, for a particular material, on the heating conditions.

It is well known that anhydrous zirconium acid phosphate shows a phase transi-

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[1] The amorphous zirconium phosphate was prepared by adding 1 liter of solution of H_3PO_4 and HCl, both 1.7 mol dm^{-3}, to 0.15 mol of $ZrOCl_2 \cdot 8H_2O$ dissolved in 1 liter of HCl, 3 mol dm^{-3}, by stirring at 80°C; after 12 h of digestion at 60–70°C, the precipitate was filtered and washed to pH 4.5, and then air-dried.

TABLE 1

Zirconium Phosphate Phases Used as Catalysts with Interlayer Distance and Surface Areas

Formula	Abbreviation	d_{002} (Å)	Surface area (m^2/g)	
			BET	Cs^+ ion exch.
$Zr(HPO_4)_2 \cdot H_2O$ (refl. 10/100)	$ZPH_2 \cdot H_2O$	7.56		
$Zr(HPO_4)_2$ 10/100 treated 180°C	ZPH_2 180°	7.43	4.20	3.70[b]
$Zr(HPO_4)_2$ 10/100 treated 300°C	ZPH_2 300°	6.80[a]	4.20	3.65[b]
$Zr(HPO_4)_2$ 10/100 treated 350°C	ZPH_2 350°	6.80[a]		
$Zr(HPO_4)_{2-x}(P_2O_7)_{x/2}$ ($x \simeq 0$) 400°C	ZPH_2 400°	6.80[a]	4.10	
$Zr(HPO_4)_{2-y}(P_2O_7)_{y/2}$ ($y \simeq 2$) 550°C	ZPH_2 550°	6.30		
L-ZrP_2O_7 treated 650°C	L-Py 650°	6.10	4.00	1.44[c]
α-ZrP_2O_7 (cubic) 1000°C	α-Py 1000°			
$Zr(HPO_4)_2 \cdot H_2O$ direct precipitation	$ZPH_2 \cdot H_2O$ dp	7.56		
$Zr(HPO_4)_2$ dp treated 300°C	ZPH_2 dp 300°	6.80[a]	1.11	1.11[b]
α-ZrP_2O_7 (cubic) 1200°C	α-Py 1200°			
$Zr(HPO_4)_2$ 10/100 300°C + Cs^+ surf. (0.37% exch. capac.)	Cs^+-ZPH_2	6.80[a]	4.20	
L-ZrP_2O_7 650°C + Cs^+ surf.	Cs^+-L-Py	6.10	4.10	
$ZrHNa(PO_4)_2$ 300°C	ZPHNa	7.33		
$ZrNa_2(PO_4)_2$ 300°C	$ZPNa_2$	7.63		
$ZrAg_{0.4}H_{1.6}(PO_4)_2$ 300°C	ZPAg-20%	6.80[a]		

[a] d_{002} at $T > 230$°C.

[b] This value is derived from the pH decrease consequent to the surface Cs^+ exchange and by considering that each hydroxyl group occupies 23.99 Å^2.

[c] This number is obtained by applying the same formula as for footnote *b* even though the material undergoes a structural change at 650°C. Its value gives a rough estimate of surface OH groups remaining after transformation of ZPH_2 to L-ZrP_2O_7, given that the BET area remains quite unaltered.

tion in the range 200–230°C. We have pointed out (*9, 14*) that the dehydration process is complete or only partial depending on whether α-$Zr(HPO_4)_2 \cdot H_2O$ is dehydrated below or above the temperature of the anhydrous phase transition. As an example, a calcination at 300°C conducted at a heating rate of 5°C/min gives a weight loss of only 0.3 mol of water per mole of exchanger, the remaining 0.7 mol being entrapped in the cavities because of the decrease of the interlayer distance (7.56 → 6.8 Å). For this reason we treated $ZPH_2 \cdot H_2O$ 10/100 or dp at 180°C for 12 h before starting with any catalytic test.

If left in air, the dehydrated samples partially rehydrate: after one week ca. 0.5 mol of water per mole of exchanger is readsorbed from ZPH_2 10/100 and only 0.15 mol from ZPH_2 dp. In both cases, we have observed that the partially rehydrated phases maintain the interlayer distance of 7.43 Å and have a degree of crystallinity lower than that of their respective anhydrous phases obtained at 180°C.

Figure 1 shows the DTA and TG curves of ZPH_2 10/100 and dp left in air at room temperature for 2 days after the materials were treated at 180°C for 12 h. The readsorbed water is lost at 200°C more easily than is the original cavity water, and the condensation process occurs in the range 350–600°C.

Figure 2 shows the weight loss kinetics of ZPH_2 10/100 of Fig. 1 at the temperatures at which the catalytic tests were performed. It can be noted that the condensation of the $\equiv$P–OH groups begins at 330–350°C, very slowly at first, and becomes more important at 380–430°C. At this latter temperature and after 12 h of heating, the material undergoes a weight loss corresponding to one-sixth of the total condensation water. The corresponding X-ray diffraction pat-

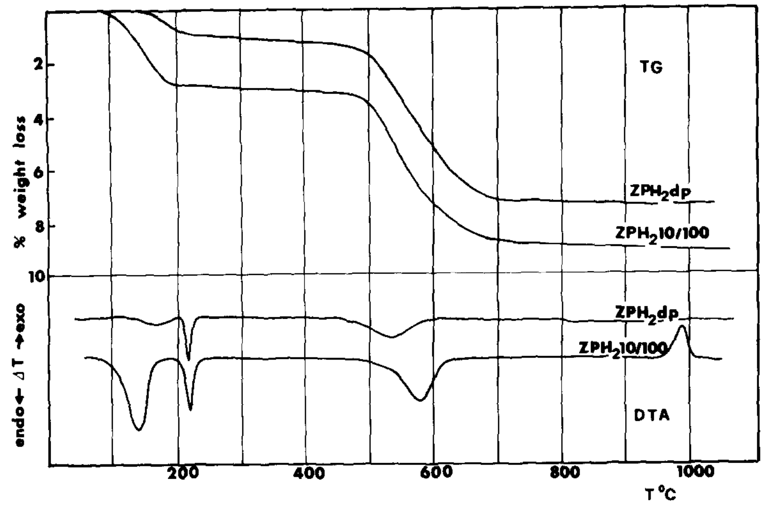

FIG. 1. Simultaneous thermogravimetric and differential thermal analysis curves of α-$Zr(HPO_4)_2$ prepared by different methods, pretreated 12 h at 180°C, and left in air for 1 week.

tern is given in Fig. 3, together with those of variously heated ZPH_2 10/100 samples. The material is a mixture of the phases labeled α' and α'' by La Ginestra *et al.* (*14*) or ζ and η by Clearfield and Pack (*15*). The condensation process is however rather limited and the pyrophosphate phase is not observed.

On further heating ZPH_2 10/100 above 500°C, layered zirconium pyrophosphate (L-Py) phases (*9*) with interlayer distance 6.1–6.3 Å are formed (Figs. 4g and h). L-Py is observed in the X-ray patterns of materials up to ca. 1000°C. In the case of ZPH_2 dp, L-Py remains up to 1200°C. Also the L-Py phases show a partial tendency to rehydrate, but to a much more limited extent

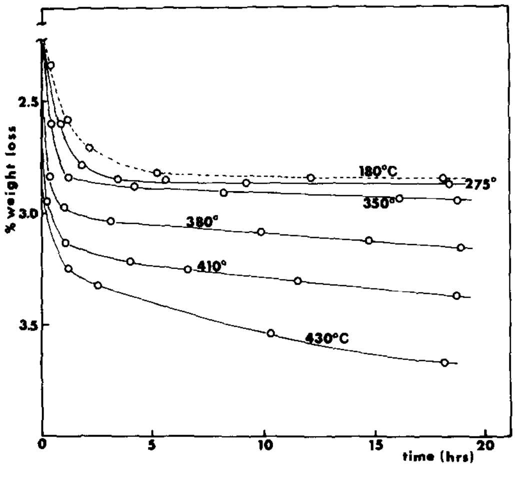

FIG. 2. Weight loss kinetics at different temperatures of $Zr(HPO_4)_2$ 10/100 of Fig. 1.

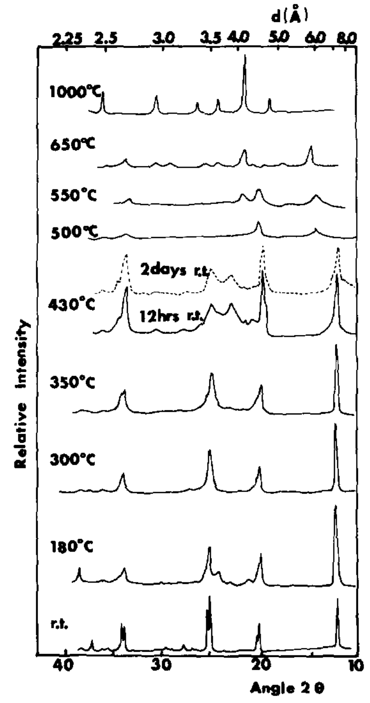

FIG. 3. X-Ray powder patterns of $Zr(HPO_4)_2 \cdot H_2O$ 10/100 after heating at different temperatures.

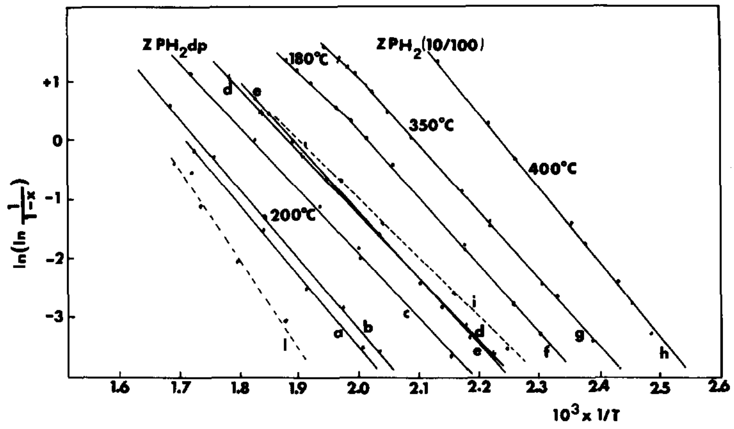

FIG. 4. Plot of ln[ln(1/1 − x)] vs $1/T$ (x = isopropanol conversion) for different $Zr(HPO_4)_2$ samples preheated at different temperatures: (a) $Zr(HPO_4)_2$ dp preheated 12 h at 200°C: 1st run, by increasing temperatures; (b) sample (a) 2nd run, by decreasing temperatures; (c) sample (a) 3rd run, by increasing temperatures; (d) sample (a) 4th run, by decreasing temperatures; (e) $Zr(HPO_4)_2 \cdot H_2O$ 10/100; (f–l) $Zr(HPO_4)_2 \cdot H_2O$ heated for 12 h at (f) 180°C, (g) 350°C, (h) 400°C, (i) 600°C; (l) 1100°C.

than ZPH_2. These data relating the progressive modifications of the zirconium acid phosphate phase with time and temperature are useful in understanding why a given thermal treatment can influence the catalytic activity of this material.

The thermal behavior of the sodium and silver zirconium phosphate phases has been reported and discussed elsewhere (*11, 17, 18*).

Surface ion exchange with Cs^+ ions. In Table 2 are given the pH values obtained by contacting 150 mg of the listed catalysts with 40 ml of a 0.1 mol dm^{-3} $CsNO_3$ solution. Before each new contact, the solids were either dried at 150°C or left wet: when the samples were not dried, the protons of the surface are almost completely exchanged with Cs^+ ions after two or three contacts. By way of contrast, for the samples dried at 150°C, after each contact an unexhausted H^+ release was observed. This behavior is a consequence either of the various rehydration–dehydration processes which cause a certain crumbling of the crystallites, or of a slow Cs^+ migration toward the internal part of the material. In either case, each process is responsible for the appearance of new surface ≡P–OH groups during each run. For this reason, the data of surface area reported in the last column of Table 1 refer to samples not dried at 150°C after each Cs^+ contact. The pH lowering observed for Cs-treated L-Py, even if limited, indicates that these condensed phases still possess a certain number of surface Brønsted sites and that the condensation at 650°C does not involve all the surface ≡P–OH groups.

Isopropanol dehydration. The catalytic dehydration of isopropanol to propene was

TABLE 2

pH Decrease Recorded after Contact of Zirconium Phosphate Phases Differently Preheated with $CsNO_3$ 0.1 mol dm^{-3} Solutions[a]

Sample (150 mg)	pH of $CsNO_3$ 0.1 M solution (40 ml) after the various contacts			
	I	II	III	IV
ZPH_2 180°[b]	4.07	5.58	5.60	
ZPH_2 180°[c]	4.07	4.40	4.95	5.35
ZPH_2 dp 180°[b]	4.58	5.45	5.57	
ZPH_2 dp 300°[b]	4.70	5.29	5.44	
L-Py 650°[b]	4.49	5.45	5.91	

[a] The 0.1 mol dm^{-3} $CsNO_3$ solution has pH 5.98.
[b] Without drying the samples after each contact.
[c] By drying the solids at 150°C after each contact.

performed on a series of zirconium acid phospahte and pyrophosphate samples derived from ZPH_2 10/100 and dp preheated at various temperatures. In Fig. 4 are reported the plots of $\ln[\ln(1/1 - x)]$ vs $1/T$ (where x is the percentage conversion of isopropanol) referred to the various catalysts.

The data have a good reproducibility for refluxed ZPH_2 preheated at 180, 350, and 400°C. This is not the case for ZPH_2 dp. Figure 4 shows that for this material the plots (a–d) shift toward those of the refluxed compound, with unchanged slope. This indicates that the activity of the dp catalyst, which is initially rather low, increases when repeated runs are performed on the same material. We believe that the water produced during the alcohol dehydration interacts with the solid, causing a progressive break-up of the crystallites with the double effect of decreasing gradually the degree of crystallinity of the material, as is confirmed from the X-ray patterns, and of making available new Brønsted sites, formerly between the layers.

Another interesting feature of Fig. 4 is that the slope of the plots in the range 200–230°C changes precisely in correspondence with the reversible phase transition of these materials, which is accompanied by a change in their interlayer distance, from 7.4 to 6.8 Å.

In Fig. 4 are reported the catalytic behaviors of L-Py and α-Py, both derived from ZPH_2. Note that L-Py has an activity almost comparable with that of ZPH_2 180°C, while that of α-Py is very poor.

When the zirconium acid phosphate phases are poisoned with Cs^+ ions (Cs^+ uptake is only 0.37% of the total ion-exchange capacity), a strong decrease in their catalytic activity is observed (Fig. 5). Since Cs^+ ions exchange practically only the hydrogens of the surface ≡P–OH groups, the experiment confirms, as already observed by other authors (*19*), that the interlayer region is not involved in the catalytic activity of the materials and that the Brønsted sites of the surface play the main role. The same conclusion holds for L-Py, which almost loses its catalytic activity when poisoned with Cs^+ ions.

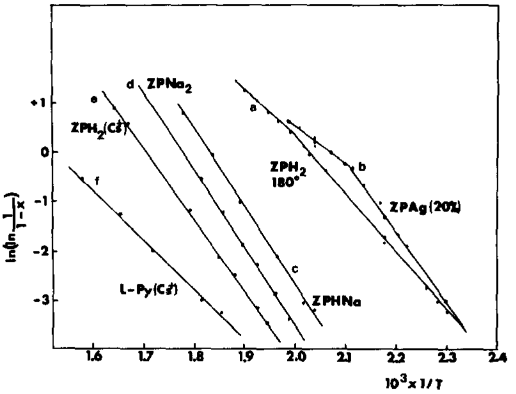

FIG. 5. Plot of $\ln[\ln(1/1 - x)]$ vs $1/T$ for isopropanol dehydration on different ion-exchanged zirconium phosphate phases: (a) $Zr(HPO_4)_2$ 10/100 preheated at 180°C, 12 h (for comparison); (b) $ZrH_{1.6}Ag_{0.4}(PO_4)_2$ 10/100 preheated at 300°C, 12 h; (c) $ZrHNa(PO_4)_2$ 10/100 preheated at 300°C, 12 h; (d) $ZrNa_2(PO_4)_2$ 10/100 preheated at 300°C, 12 h; (e) $Zr(HPO_4)_2$ 10/100 preheated at 300°C, 12 h, poisoned with $CsNO_3$ solution; (f) $Zr(HPO_4)_2$ 10/100 preheated at 650°C 12 h, poisoned with $CsNO_3$ solution.

In Fig. 5 are also given the plots referring to zirconium phosphate materials exchanged with Ag^+ or Na^+ ions. Particularly interesting is the catalytic activity of ZPAg-20%, which is higher than that of ZPH_2 180°C. As for the pure hydrogen forms, the slope changes in correspondence with the temperature (170°C) at which this material also exhibits a reversible anhydrous phase transition (*11*).

The apparent activation energy values of the isopropanol dehydration, for the various materials employed, are given in Table 3. By operating with different feed flows, we have observed that this reaction obeys first-order kinetics (*20*). In the case of plots with a change of slope, the two measured values of apparent activation energy are reported.

1- and 2-butanol dehydration. Dehydration experiments on 1- and 2-butanol were carried out on ZPH_2 preheated at 300°C as a function of temperature. The results are reported in Figs. 6a and b. The dehydration

TABLE 3

Apparent Activation Energies for Isopropanol Dehydration Measured for Different Zirconium Phosphate Phases

Catalyst	E_a^* [Kcal]
$ZPH_2 \cdot H_2O$ 10/100	11.46 ± 0.5
ZPH_2 180°	11.43 ± 0.4/9.10 ± 0.4 (above 200°C)
ZPH_2 300°	11.20 ± 0.3/9.40 ± 0.5 (above 200°C)
ZPH_2 350°	11.10 ± 0.3/9.40 ± 0.5 (above 200°C)
ZPH_2 400°	12.30 ± 0.8
L-Py 650°	10.20 ± 0.3
α-Py 1100	15.20 ± 0.8
$ZPH_2 \cdot H_2O$ dp	11.30 ± 0.6
ZPH_2 dp 200°	12.22 ± 0.5
ZPH_2 dp 300°	10.80 ± 0.6
Cs^+–ZPH_2 300°	13.70 ± 0.3
Cs^+–L-Py	9.37 ± 0.4
ZPHNa	14.90 ± 0.5
$ZPNa_2$	15.10 ± 0.5
ZPAg-20%	13.30 ± 0.6/7.05 ± 0.5 (above 200°C)

process goes to completion for both alcohols above 350°C. The catalyst not only gives 1- and 2-butene (derived directly from the two corresponding alcohols) but also their respective isomerization products, 2-butene (*cis* and *trans*) and 1-butene. Since the isomerization products obtained above 350°C, when the alcohol conversion is complete, increase with an increase in the temperature at the expense of 1- and 2-butenes, which are primarily formed, this could be indicative that the strength of the Brønsted sites also increases in parallel.

Isomerization of 1-butene. This reaction has been chosen because the absence of water in the process should prevent complications which arise from the interaction between water and catalyst during the dehydration of alcohols and should give more correct information on the strength of the acidic sites of the differently preheated zirconium phosphate phases. The tests were performed either by increasing the temperatures at a fixed flow feed or by varying the contact times at a fixed temperature.

In Fig. 7 are reported the percentages of reactant left (1-butene) and products formed (*cis*-, *trans*-2-butene and isobutene) at increasing temperatures, for three samples (1g) of ZPH_2 10/100 pretreated at three temperatures: 300, 400, and 650°C (at this latter temperature the catalyst is L-Py). Given that the surface ≡P–OH groups in the first two samples are about three times those present in L-Py (see Table 1), Fig. 7 also shows the results obtained by using 3 g of L-Py, in order to allow the reactant to encounter approximately the same number of active sites.

cis- and *trans*-2-butene are the main products of the isomerization of 1-butene, although small amounts of isobutene are also formed on the samples pretreated at 400 and 650°C. The results show that the catalysts have mainly acidic sites of medium strength (*6*), and that by increasing the temperature of the thermal pretreatment, some active sites become stronger, as indicated by the formation of isobutene. The active sites are only surface sites: on poisoning the three samples with Cs^+ ions, the isomerization of 1-butene is completely

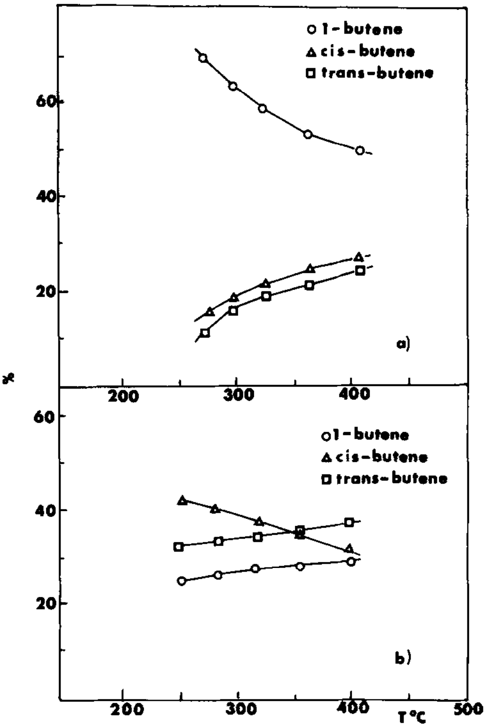

FIG. 6. Relative amounts of butenes formed at different temperatures with the dehydration of (a) 1-butanol and (b) 2-butanol on $Zr(HPO_4)_2$ 10/100 pretreated at 300°C.

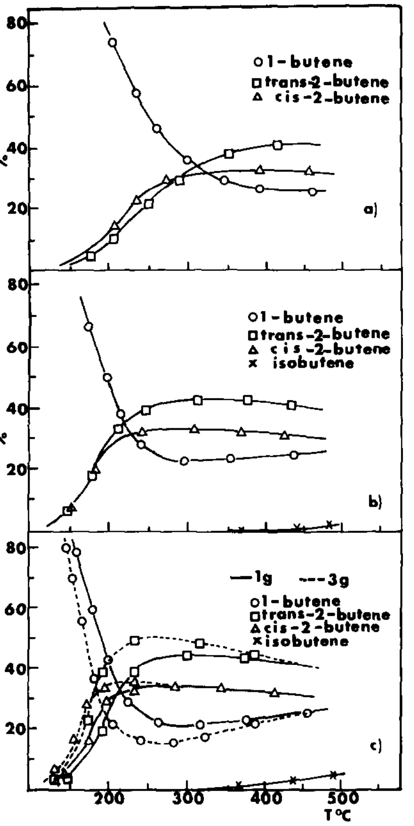

FIG. 7. Isomerization products of 1-butene on $Zr(HPO_4)_2$ 10/100 preheated 12 h at (a) 300°C (1 g), (b) 400°C (1 g), (c) 650°C (1 and 3 g).

annihilated in the case of L-Py and becomes minimal for the other two catalysts.

Figure 7 clearly shows that the conversion of 1-butene increases as the temperature of the thermal pretreatment of the catalyst is increased. Furthermore, the most active phase is L-Py. In fact when L-Py and ZPH_2 400° are used in the same amount (1 g) their activity is comparable, although L-Py possesses only one-third of the surface sites of ZPH_2 400. This indicates that the L-Py active sites are stronger than those of the other ZPH_2 materials, as is also confirmed by the slightly higher formation of isobutene. By increasing the temperature of the experiment, ZPH_2 pretreated at 300 and 400°C tends to exhibit the same activity as L-Py, the phase to which they slowly transform when used above 350–400°C.

Figure 7 also shows that the *cis*/*trans* ratio is >1 at low temperature and <1 at higher temperature; we observe that the temperature at which this ratio is equal to 1 decreases from ZPH_2 300° to L-Py 650°; i.e., the inversion temperature decreases as the acidic sites of the catalyst become stronger.

A different comparison is presented in Fig. 8 which reports the percentage of different butenes obtained by varying the contact time on the same amounts (1 g) of the above-mentioned catalysts, at a temperature of 300°C. The catalysts reflect an acidic strength following the order: $cat_{650} > cat_{400} > cat_{300}$, as found in the previous experiments (Fig. 7).

DISCUSSION

Type and strength of the acid sites. From the results obtained for the different acid-catalyzed reactions, it can be inferred that the catalytic activity of the various materials (zirconium hydrogen phosphate or zirconium pyrophosphate phases) is confined to their surface and that it is mainly due to the Brønsted sites present there. This assessment is clearly demonstrated with the experiments performed on the Cs-poisoned catalysts, in which the catalytic activity is

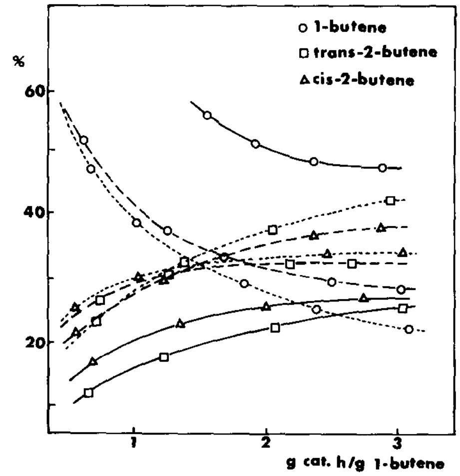

FIG. 8. Isomerization products of 1-butene at 300°C for different residence times on $Zr(HPO_4)_2$ 10/100 preheated 12 h: —, at 300°C; ---, at 400°C; · · ·, at 650°C.

completely annihilated, as in the case of isomerization of butenes on Cs^+–L-Py, or severely decreased as in the other cases.

The residual low catalytic activity observed in the alcohol dehydration on Cs^+–ZPH_2 has been discussed by other authors (*19*). We believe it could be due to new Brønsted sites generated either from the crumbling of the crystallites after interaction with water, as discussed above, or from some Cs^+ diffusion into the exchanger and consequent migration of H^+ on the surface or to some Lewis sites not poisonable by Cs^+ ions. Concerning the very weak activity shown by Cs^+–L-Py in the same reaction, we suggest it could be connected to the formation of some ≡P–OH groups originating from the hydrolysis of P–O–P bridges, caused by the water evolved during the catalytic process at temperatures >200°C. A break-up of the crystallites may occur during the drying of the Cs-poisoned L-Py at 150°C, but this temperature is too low to cause P–O–P hydrolysis. Also in this case the existence of some Lewis sites cannot, at present, be excluded.

In the case of the isomerization of butene, where no water is produced, no activity is shown by Cs^+–L-Py, and only a very low activity is observed with Cs^+–ZPH_2. In the latter case the crumbling of the crystallites, occurring on heating, is now the only effect that can provide some new surface ≡P–OH groups.

Further confirmation that the active sites are only on the surface of the materials comes from the behavior of ZPHNa, $ZPNa_2$, or α-ZrP_2O_7 in the dehydration of isopropanol (Fig. 6). On comparing the results obtained with ZPHNa (where 50% of the ≡P–OH groups with respect to ZPH_2 are present in the whole solid) and Cs-poisoned ZPH_2 180°C (ca. 0.38% of the total ≡P–OH groups are exchanged with Cs^+ ions and only on the surface), the latter material is much less active although it still possesses 99.6% of the initial Brønsted sites.

The $ZPNa_2$ or α-Py phases should not be able to catalyze the mentioned reaction. Notwithstanding this, they show a detectable, although low, catalytic activity which can derive from the presence of some surface Brønsted sites or some Lewis sites. In the case of $ZPNa_2$, the Brønsted sites can be generated by partial hydrolysis or surface H/Na ion exchange during the washing of the product when it is prepared. In the case of α-Py, as for L-Py, they may be residual surface Brønsted groups not involved in the condensation process, probably because they are too distant to give P–O–P bridges. The presence of surface ≡P–OH on both the pyrophosphate phases has been demonstrated by the decrease in pH observed when these materials are contacted with Cs^+ solutions. The more marked effect found for L-Py indicates that this catalyst possesses more surface Brønsted sites than does α-Py.

In their investigation on the catalytic dehydration of cyclohexanol, Clearfield and Thakur (*19*) also conclude that the active sites of ZPH_2 are only on the surface.

As regards the nature of the surface sites, on the basis of the above arguments, we can infer that in the case of butene isomerization only the P–OH groups are the active sites since with Cs^+–L-Py no activity is detected, and the low activity observed with Cs^+–ZPH_2 can be due to new Brønsted groups connected with the crumbling of the crystallites. This conclusion agrees with the accepted mechanism of the butene isomerization occurring via a secondary butyl-carbonium ion (*21*). In the case of dehydration of isopropanol we must believe that the surface active sites are mainly Brønsted groups because of the strong decreasing of activity of the Cs-poisoned catalysts. For these latter materials, we have not, at the moment, sufficient information in order to attribute the residual low activity to new Brønsted sites (generated either by the break-up of the crystallites or the water interaction at high temperature) or to some Lewis sites present on the surface.

The method generally adopted to give a quantitative evaluation of the surface Brønsted sites and a measure of their strength, i.e., *n*-butylamine titration using Hammett indicators (*19, 22*), cannot be used for the ZPH_2 materials, because in this case the titration also involves the ≡P–OH groups lying between the layers, and intercalation compounds are obtained (*23, 24*). This method is probably useful only for L-Py. We believe that for our catalysts a valid indication on the strength of their surface acid sites can be obtained from their performance in the isomerization of butene. Therefore, since ZPH_2 materials preheated below 400°C mainly give rise to configuration and double bond isomerizations, they can be classified as catalysts possessing active sites of medium strength. In the case of ZPH_2 preheated at 400°C or L-Py, which in addition are capable of giving small amounts of isobutene (i.e., a skeleton isomerization), their surface P–OH groups may be classified as being medium-high strength sites (*6*).

Effect of the thermal pretreatment. The continuous increase in the strength of surface acid sites by increasing the temperature of the thermal pretreatment of the zirconium phosphate phases is a subject treated in previous works (*19, 22*) but, in our opinion, no satisfactory explanations have yet been put forward. We are convinced that the cause of this behavior must be sought in the modification of the structure and chemistry of the materials during the thermal pretreatment, and even during the catalytic tests.

From the isothermal thermogravimetric data of Fig. 2 it can be noted that by heating at 330°C, ZPH_2 undergoes a continuous weight loss, which becomes more marked as the temperature is increased. The weight loss is obviously due to the partial condensation of the ≡P–OH groups (mainly between the layers) to pyrophosphate. The concomitant increase of the surface sites strength may be ascribed to the formation of "islands" of layered phase containing a certain number of P–O–P bridges between the layers, able to confer a greater ionic character on the surface acid sites.

The increase in the strength of Brønsted sites with the transformation to the pyrophosphate phase has been also observed by Segawa *et al.* (*16*) in a paper which appeared during the writing of this paper. These authors report data concerning the catalytic behavior of η- and α-$Zr(HPO_4)_2$, both materials showing a strong increase of the catalytic activity in the isomerization of 1-butene and of the *trans*/*cis* ratio in the same temperature range at which the condensation to pyrophosphate occurs. Although η-$Zr(HPO_4)_2$ possesses a structure different from that of the α-compounds, and their pyrophosphate phases are different from our layered phase, we agree with the conclusion that the P–O–P bond formation must involve an increase of the strength of the surface ≡P–OH Brønsted sites.

Our preliminary data regarding the catalytic activity of the isostructural Ge, Ti, and Sn acid phosphates (*5*) also show that when these materials are transformed into the respective layered pyrophosphate phases they become more active for the acid-catalyzed reactions. This confirms that, although less numerous, the acidic surface sites in the latter phases must be stronger than those present on the hydrogen phosphate phases.

The partial formation of P–O–P bridges between the layers makes difficult the complete restoration of the starting ZPH_2 with interlayer distance of 7.43 Å: the X-ray pattern, taken at room temperature, of a sample of ZPH_2 heated at 430°C for 12 h, where one-sixth of the condensation water is lost (Fig. 2), shows the simultaneous presence of the predominant anhydrous ZPH_2 with interlayer distance 7.43 Å and, in a lesser amount, of the α''- or η-phase, the existence of which is revealed by its stronger reflexion at 3.8 Å. The presence of α''- or η-phase, which is stable only at $T > 230°C$ and should not be observable in a spectrum taken at room temperature because it reverts into the 7.43 Å phase, is justified only because some interlayer P–O–P bridges are formed. Our X-ray data are in agreement with those found by Frianeza and Clearfield

(*25*) in the case of mixed titanium–zirconium hydrogen phosphate phases heated at 300–350°C. These authors observed the stabilization of the η-phase, at room temperature, which is explicable only in terms of a partial condensation of the acid phosphate phases to pyrophosphate.

Catalytic activity of ion-exchanged materials. The catalytic activity of ZPH_2 is affected when the chemical composition is varied by ion exchange. The negative effect of the alkali ions such as Cs^+ and Na^+, connected with the decrease in the number of surface Brønsted sites, has been widely discussed.

By way of contrast, the catalytic activity of ZPH_2 converted with Ag^+ up to 20 or 50% of the exchange capacity is comparable with that of pure ZPH_2, preheated at the same temperature. Furthermore the activation energy values in the dehydration of isopropanol are slightly lower than those calculated for ZPH_2. We explain this behavior by invoking the fact that, at $T > 100°C$, Ag^+ is slowly reduced by isopropanol. Silver atoms may form near the Brønsted sites and they would not be entirely inert in the isopropanol dehydration process; they could play some role in eliminating H_2O from the catalyst surface. Indeed, we have already observed (*26*) that the condensation process of the hydrogen phosphate groups occurs at lower temperature when Ag is present in the materials under reducing atmosphere of H_2.

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