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Catalytic Studies on the Dehydration of Cyclohexanol by Crystalline Titanium Phosphate and Mixed Titanium–Zirconium Phosphates

I. Effect of Thermal Phase Changes on Catalytic Activity

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Crystalline α-titanium phosphates, $Ti(HPO_4)_2 \cdot H_2O$, and solid solutions of titanium–zirconium phosphates were prepared and their activity in the dehydration of cyclohexanol examined. The α-phases were found to lose 1 mol of water at slightly above 100°C and convert to the ζ-phase. A second, reversible phase change, to form η-phases, occurs at about 250°C while condensation of the monohydrogen phosphate groups takes place from 300 to 400°C. When sufficient —OH groups are lost, the η-phases do not revert to the ζ-phases on cooling. However, the alcohol dehydration reaction catalyzed by the η-phases apparently restores sufficient hydroxyl groups to allow the catalysts to reform the low temperature ζ-phases. There seems to be no correlation of catalytic activity with either the Ti content of the catalysts or their surface areas. However, all of them were found to be more active than α-zirconium phosphate.

I. INTRODUCTION

Orthophosphates of aluminum and boron are known to catalyze reactions such as dehydration, isomerization, and dehydrogenation (*1*). The catalytic activity of these compounds stems from their acidic nature and a great deal of effort has been expended in characterizing the active sites. In contrast, very little is known about the acidic properties of the group(IV)B orthophosphates of general formula $M(IV)(HPO_4)_2$. These compounds have layered structures and behave as ion exchangers (*2*). Their ion-exchange behavior does not depend upon the p*K* of the contained protons but is governed more by the interlayer distances and the geometry of the fixed groups (*3, 4*). However, these compounds do exhibit catalytic behavior either in the hydrogen (*5–13*) or the cation-exchanged forms (*14–17*). Therefore, it is of interest to explore the role of the acid sites in these compounds.

Hattori *et al.* (*18*), employing the butylamine titration (Benesi) method, determined that $Zr(HPO_4)_2$ contained both weak and strong acid sites and that Brønsted acid sites were responsible for the dehydration of 1-butanol (*19*). Clearfield and Thakur (*20*) confirmed the distribution of acid sites found by Hattori *et al.* and showed that the rate of dehydration of cyclohexanol was directly proportional to the number of P—OH groups on the surface (*21*). This rate deviated from linearity only for catalysts with low surface areas.

α-Titanium phosphate, $Ti(HPO_4)_2 \cdot H_2O$, is isomorphous with α-zirconium phosphate (*2, 22*) and also exhibits similar ion exchange behavior and acidic properties in its catalytic behavior (*23–27*). A second form of this phosphate known as γ-TiP, is also under study and will be reported upon later.

We have undertaken a fundamental study of the acidic properties of the group IVB phosphates. In this paper, we examine the behavior of crystalline titanium phosphates and mixed titanium–zirconium phosphates in catalyzing the dehydration of cyclohexanol. It will be shown in what follows that α-titanium phosphate undergoes phase changes, as well as dehydration to pyrophosphate, at temperatures within the

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range at which alcohol dehydration occurs. Therefore it was necessary to examine the nature of these phase changes and to determine their effect on the catalytic reactions.

II. EXPERIMENTAL PROCEDURE

Preparation and characterization of catalysts. α-Titanium phosphate (α-TiP) was prepared by refluxing a gel in 12M H_3PO_4 for 250 h (*22*). This procedure was similar to that employed for α-zirconium phosphate (α-ZrP) (*2*). The crystalline mixed titanium–zirconium phosphates were prepared as described previously (*22*) with titanium contents of 20, 33, and 80 mol%. Neutron activation analysis was performed on the samples to obtain experimentally the Ti : Zr ratios in the refluxed solids. Water contents were obtained both by TGA and static weight loss. X-Ray diffraction patterns were run with a Seifert-Scintag automated powder diffractometer(PAD-II) using Ni-filtered Cu$K\alpha$ radiation. Accurate peak positions were obtained using program PKSRCH (*28*).

Surface area determinations. Ammonium ion is known not to exchange with the interior protons of α-ZrP but to displace only those on the surface (*29*). Thus, the exhaustive treatment of α-ZrP samples with 0.1 *N* NH_4Cl can be used to obtain their surface areas from the number of protons liberated (*30, 31*). α-Titanium phosphate has even smaller openings into the interlayer space than does α-ZrP because the smaller Ti(IV) ion produces a closer approach of phosphate groups (*32*). Therefore, the ammonium ion surface titration procedure was applied to the determination of surface areas of α-TiP and the mixed titanium–zirconium phosphates. These were checked by the BET method. Surface areas of the catalysts were also determined after heat-treating at several temperatures as well as at room temperature.

Catalytic studies. The reactor system was of conventional design with a motor-driven syringe liquid feed, an electrically heated plug flow reactor, a liquid sample collector, and a trap to condense volatile products. The U-tube stainless-steel reactor had a 6-mm internal diameter and was 200 mm long. A known amount of catalyst (ca. 250 mg) was accurately weighed and loaded into the reactor. It was heated for a sufficient period of time (24 h) prior to the catalytic runs at the desired temperature by means of a furnace controlled to ±1°C by a Barber Coleman temperature controller. Helium was passed through a molecular sieve, drierite, and an oxygen trap before it flowed through the reactor. The catalytic runs were made at the same pretreatment and reaction temperatures, which ranged from 250 to 400°C, in order to observe the effect of thermal phase changes on the catalytic activity in the dehydration of cyclohexanol.

Cyclohexanol (5 ml) was pumped over the catalyst at atmospheric pressure in a He carrier for each run. Different cyclohexanol flow rates were used and the condensed products were collected and analyzed using a Hewlett–Packard 5830 A gas chromatograph as described earlier (*20*).

RESULTS

Characterization of α-TiP and $Ti_{1-x}Zr_xP$ *catalysts.* Table 1 lists the neutron activation analyses data, weight loss data, and the corresponding formulas of the compounds. Agreement between the theoretical weight loss calculated for the expected formula and the total loss on ignition values indicates near quantitative precipitation of both titanium and zirconium in the mixed phosphates. The X-ray diffraction patterns of the three mixed phosphates, as well as α-TiP, has previously been published (*22*) and the similarity in behavior of the 80 mol% Ti-containing compound ($Ti_{0.8}Zr_{0.2}P$) to α-TiP and the 20 mol% solid ($Ti_{0.2}Zr_{0.8}P$) to α-ZrP established. X-Ray patterns for $Ti_{0.33}Zr_{0.67}(PO_4)_2\ H_2O$ ($Ti_{0.33}Zr_{0.67}P$) showed the presence of two phases, one rich in Zr and the other in Ti (*22*).

Water losses of the mixed phosphates, as determined by thermogravimetric analysis,

TABLE 1

Neutron Activation Analyses and Weight Loss Data for Crystalline Titanium–Zirconium Phosphates

Initial Ti–Zr mole ratio	Expected formula	Weight loss (%)			NAA for Ti (mol%)
		TGA	LOI	Theoretical	
1–4	$Ti_{0.20}Zr_{0.80}(HPO_4)_2 \cdot H_2O$	12.0	12.2	12.3	17.2
1–2	$Ti_{0.33}Zr_{0.67}(HPO_4)_2 \cdot H_2O$	12.5	12.8	12.6	33.4
4–1	$Ti_{0.80}Zr_{0.20}(HPO_4)_2 \cdot H_2O$	13.7	13.7	13.6	78.2
∞	$Ti(HPO_4)_2 \cdot H_2O$	14.1	14.0	13.97	100.0

are shown in Fig. 1. A similar curve for $Ti(HPO_4)_2 \cdot H_2O$ is included. Weight losses can be interpreted in the same manner as has been done for α-ZrP (*33*). One mole of water of crystallization is lost above 100°C and a second mole at higher (~400°C) temperatures. The solids then have the compositions corresponding to the pyrophosphates, TiP_2O_7 or $Ti_xZr_{1-x}P_2O_7$, but crystallization to the pyrophosphate does not occur until the solids are heated to much higher temperatures. As will be shown subsequently, weakly crystalline, almost amorphous, phases are obtained after the second water loss.

α-ZrP is known to undergo a phase change at 100°C to ζ-ZrP which has an interlayer spacing of 7.41 Å. This phase in turn converts to η-ZrP at about 230°C with shrinkage of the interlayer distance to 7.1 Å (*33*). Since the particular phase present in the dehydration reaction may have a significant influence on catalytic behavior, X-ray patterns were taken of the present catalysts after heating to different temperatures to determine whether similar changes occur. The results are collected in Table 2. Heating α-TiP to 250–300°C resulted in its permanent conversion to ζ-TiP while above this temperature the phase observed at room temperature was η-TiP.

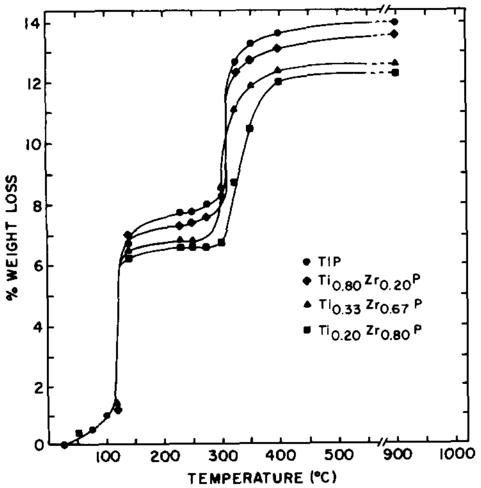

FIG. 1. Dehydration curves for α-titanium phosphate (12:250) and the mixed titanium–zirconium phosphates.

These results are in some disagreement with those reported by La Ginestra *et al.* (*34*) who found that the water of hydration is lost slightly above 100°C with conversion to ζ-TiP. This phase was in turn converted to η-TiP at 260°C, but this latter phase change was found to be reversible just as it is in the α-ZrP system. The apparent discrepancy between our results and those of La Ginestra can be explained on the basis of the reversibility of the zeta–eta phase change. Above 250°C the stable phase is η-TiP, but when the samples are cooled to room temperature, they revert to ζ-TiP. Each of the X-ray patterns for ζ-TiP obtained by heating in the range of 250–300°C contained a low intensity reflection at 4.28 Å which is the most intense reflection in the η-TiP pattern. Samples of TiP which had been heated above 300°C retain the η-TiP X-ray pattern on cooling to room temperature because they have lost a significant amount of water via phosphate condensa-

TABLE 2

Phases Formed by α-TiP and the Mixed Titanium–Zirconium Phosphates at Elevated Temperatures before and after Use as a Dehydration Catalyst

Temp (°C)	Phases formed by catalyst							
	α-TiP		$Ti_{0.8}Zr_{0.2}P$		$Ti_{0.33}Zr_{0.67}P$		$Ti_{0.2}Zr_{0.8}P$	
	Before	After	Before	After	Before	After	Before	After
250	$\zeta + \eta$(Tr)	ζ	$\zeta + \eta(5\%)$	ζ	ζ	ζ	ζ	ζ
275	$\zeta + \eta$(Tr)	ζ	$\zeta + \eta(\sim 10\%)$	ζ	ζ	ζ	$\zeta(25\%) + \eta$	$\zeta + \eta(\sim 5\%)$
300	$\zeta + \eta$(Tr)	ζ	$\zeta + \eta(\sim 10\%)$	ζ	ζ	ζ	$\zeta(\sim 10\%) + \eta$	$\zeta + \eta(\sim 10\%)$
325	η	$\zeta + \eta$	η	ζ	am[a]	$\eta + \zeta$	$\zeta(5\%) + \eta$	$\eta + \zeta(\sim 25\%)$
350	η	$\zeta + \eta$	η	ζ	am	η	η	η
400	η	η	η	η	am	η + am	η + am	η

[a] Amorphous.

tion, thus rendering the phase change irreversible.

The same general trend is noted with the mixed titanium–zirconium phosphates. However, for $Ti_{0.33}Zr_{0.67}P$ heating above 300°C destroys most of the crystallinity while with $Ti_{0.2}Zr_{0.8}P$ more of the η-phase is obtained at lower temperatures, which is more in agreement with the behavior of pure α-ZrP.

The surface area of the catalysts, as a function of heating temperature, are shown in Fig. 2. At first the results may seem curious, but they can be rationalized on the basis of the phase changes accompanying the heating process. An increase in surface area accompanies heating the samples to 250°C and this may be the result of the breakup of the crystallites caused by the $\alpha \rightarrow \zeta$ phase change. Further heating reduces the surface area somewhat but a second increase, for all samples except $Ti_{0.2}Zr_{0.8}P$, occurs as a result of the $\zeta \rightarrow \eta$ phase change. We also have no explanation at present for the apparently anomalously high surface areas of this sample after heating to 250 and 300°C, although these values were checked twice.

Cyclohexanol dehydration. Cyclohexanol dehydration studies were carried out for each of the four catalysts as a function of temperature. The catalysts were held at the reaction temperature in a flow of helium for 24 h before contacting the alcohol. Under the conditions of our experiments cyclohexene and water were the only detectable products. The results are shown in Figs. 3–6 and Table 3. It is seen that there is a steady increase in the percentage of dehydration with increasing temperature at all contact times except for $Ti_{0.2}Zr_{0.8}P$. This catalyst exhibited a marked decrease in ac-

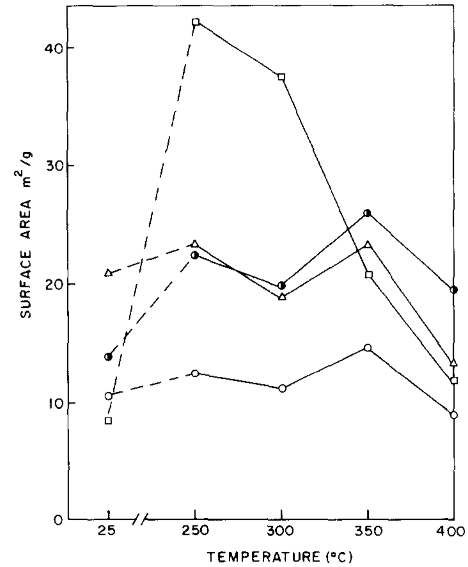

FIG. 2. Surface area as a function of dehydration temperature for α-titanium phosphate 12:250 ○, $Ti_{0.8}Zr_{0.2}P$ ◑, $Ti_{0.33}Zr_{0.67}P$ △, $Ti_{0.2}Zr_{0.8}P$ □.

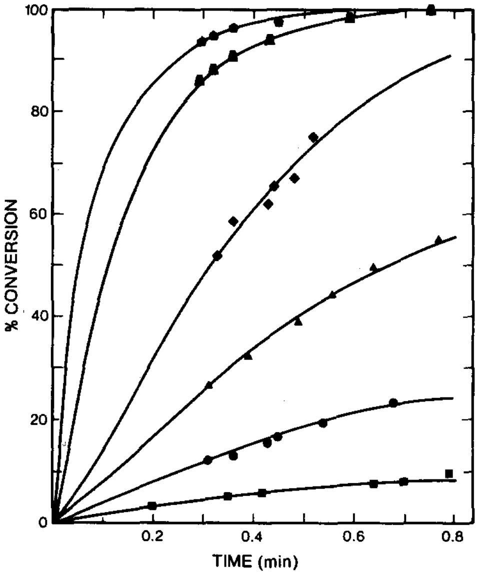

FIG. 3. Percentage conversion versus contact time for α-titanium phosphate (12 : 250) for dehydration of cyclohexanol at different temperatures. 250°C ■, 275°C ●, 300°C ▲, 325°C ◆, 350°C ▲, 400°C ⬟. Catalysts were pretreated at the same temperature as the reaction temperature.

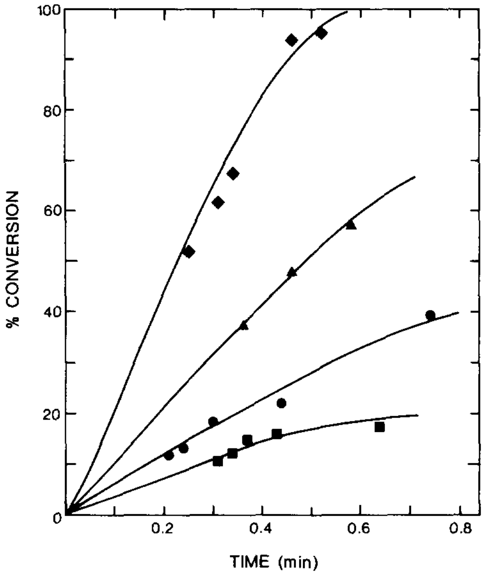

FIG. 5. Percentage conversion versus contact time for $Ti_{0.33}Zr_{0.67}P$. Conditions and symbols same as for Fig. 3 except highest temperature was 325°C.

tivity at 400°C. This catalyst also suffered the largest decrease in surface area at 400°C. The numbers in parentheses in Table 3 are the percentage conversions divided by the surface area. On the basis of per unit surface area, it is seen that α-TiP is the most effective catalyst.

There appears to be no regular progres-

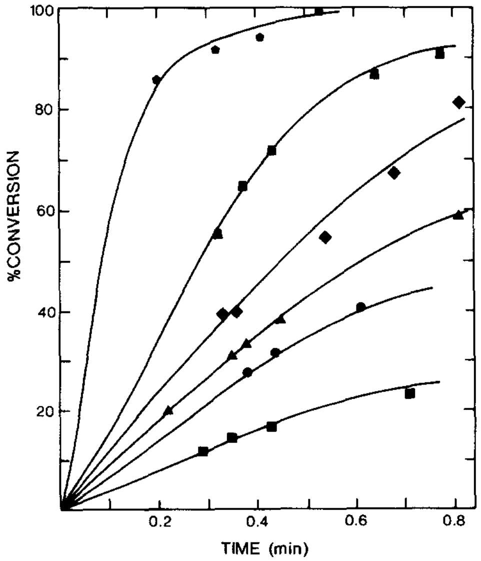

FIG. 4. Percentage conversion versus contact time for $Ti_{0.8}Zr_{0.2}P$. Conditions and symbols same as for Fig. 3.

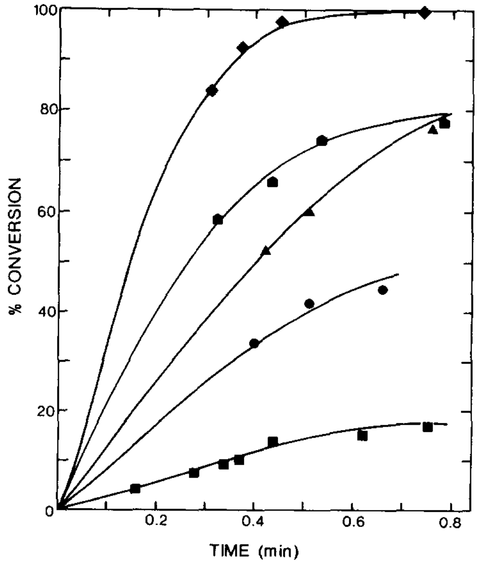

FIG. 6. Percentage conversion versus contact time for $Ti_{0.2}Zr_{0.8}P$. Conditions and symbols same as for Fig. 3 except that run at 350°C is omitted.

TABLE 3

Percentage Conversion of Cyclohexanol over TiP(12 : 250) and $Ti_{1-x}Zr_xP$ Catalysts at a Contact Time of 0.40 min for the Same Pretreatment and Reaction Temperature[a]

Catalyst	Temperature (°C)					
	250	275	300	325	350	400
TiP(12 : 250)	6(0.5)	16(1.4)	34(3)	62(4.8)	93(6.4)	97(10.1)
$Ti_{0.80}Zr_{0.20}P$	16(0.7)	28(1.3)	35(1.8)	45(2.0)	68(2.6)	96(4.9)
$Ti_{0.33}Zr_{0.67}P$	15(0.6)	23(1.1)	42(2.2)	84(4.0)	100(4.3)	100(7.5)
$Ti_{0.20}Zr_{0.80}P$	12(0.3)	34(0.8)	50(1.3)	94(3.2)	100(4.8)	66(5.5)

[a] These values were taken from data plotted in Figs. 3–6.

sion of catalyst activity increase with either surface area or Ti content. Furthermore, for these samples most of the P—OH groups should have been condensed to P—O—P linkages at 400°C, yet the dehydration ability of the catalysts remained high. Thus active sites, other than of the Brønsted type, may also be present in significant numbers. Therefore, X-ray examination of the catalysts after they had been used in the dehydration reactions was carried out to determine which phases were now present. The results are given in Table 2. They reveal a greater prevalence of the ζ-phase at the higher temperatures after reaction than was present in the catalysts prior to reaction and a greater overall crystallinity of the catalysts. It seems likely that the water generated during the reaction substantially rehydrates the catalyst, so that a greater amount of Brønsted acid sites are present than would have been expected from the water loss curves in Fig. 1. This facilitates the $\eta \rightarrow \zeta$ transition on cooling.

DISCUSSION

α-TiP and the mixed titanium–zirconium phosphates were found to undergo the same two phase changes as α-ZrP. However, the major difference in the titanium-containing compounds is their loss of water through condensation of monohydrogen phosphate groups well below 400°C. Since with α-ZrP it was shown that the major active dehydration sites are the Brønsted acid P—OH groups, it might be expected that the titanium containing catalysts would be less active than zirconium phosphate. Yet quite the opposite is true. This is partly due to regeneration of the P—OH groups during the reaction through contact of the surface with steam. This hypothesis needs independent corroboration but appears to be on firm ground since poorly crystalline η-phases obtained by prereaction heating treatment are converted to highly crystalline phases after the catalytic reaction. Regeneration of the P—OH groups is also to be inferred from the fact that the curves in Figs. 3–6 are S-shaped. The initial accelerating rate at low contact times could result from more active sites being generated with increased yield which produces a higher water vapor pressure. As a result of the Brønsted site regeneration we may assume that there are roughly equal numbers of P—OH groups in α-TiP and α-ZrP and the enhanced activity results from the greater acidity of the TiP sites (Brønsted or Lewis). The question as to the relative strength of the Brønsted acid sites is under investigation via a calorimetric study of butylamine uptake by the catalysts.

There seemed to be no correlation of activity as a function of titanium content of the catalysts, either as is or per unit of surface area. It is very likely that as the water splits out of the catalyst highly active sites remain on the surface either as hydroxyl groups, coordinatively unsaturated Ti^{4+} or imperfectly formed pyrophosphate groups. Obviously a better characterization of these surfaces is needed to place the reactions on a more quantitative basis.

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