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The Acidity of Zirconium Phosphates in Relation to Their Activity in the Dehydration of Cyclohexanol[1]

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Three samples of zirconium phosphate varying in crystallinity from amorphous to highly crystalline were prepared and characterized as to surface area, surface acidity, and activity in cyclohexanol dehydration. The number of strong acid groups was found to increase with increased temperature of pretreatment of the solids, except for the amorphous exchanger. For that solid condensation of hydroxyl groups is significant at temperatures of 200–400°C reducing the surface acidity. The dehydration reaction was found to be first order in alcohol concentration and to increase in rate with increase in the number of strong acid groups. The reaction was poisoned by the exchange of surface protons with Cs^+ or introduction of quinoline into the feed stream. Thus, the active sites must be the monohydrogen phosphate protons. However, a small amount of activity is due to a second site probably of the Lewis acid type.

INTRODUCTION

The use of metal phosphates as catalysts (*1–15*) in various reactions viz. dehydration, isomerization, polymerization, alkylation, etc. has received considerable attention. Although, the fact that the metal phosphate surface possesses acid sites capable of taking part in the catalytic process has been demonstrated by several chemical and physicochemical techniques (*1, 8, 16–19*), the information concerning the existence of both Bronsted and Lewis acidity is limited. Catalytic activity, especially in dehydration and cracking reactions of various catalysts including metal phosphates (*1, 19–23*), is related to the acid strength of these solids. Hence, an understanding of the acidic nature of a solid surface is of great importance in the study of acidic catalysts for the above-mentioned reactions. Several excellent reviews concerning the determination of acidity of solid catalysts have been published (*22, 24–26*) which critically discuss various methods, e.g., amine titrations using Hammett indicators, ir spectroscopy, adsorption of bases, etc. The so-called Benesi method (*27, 28*) which involves the titration of a solid with *n*-butylamine in benzene or isooctane, was modified by Bertolacini (*29*), in which he used an ultrasonic vibrator to reduce the duration of the experiment from 2 days to 0.5 hr. Deeba and Hall (*30*) have recently devised an alternative method for characterizing site energy distribution.

Another method (*31–36*), which has frequently been employed by various workers, consists of the determination of the amount of base required to poison the catalytic activity for a model reaction. This method is therefore referred to as a catalytic titration. Quinoline titrations of zeolites have gained a considerable importance in the past few years (*31–36*). Danforth *et al.* (*37*) carried out the titration by adding varying amounts of alkali hydroxide solutions to aqueous solutions of cracking catalysts. The solids were then dried, activated, and tested for their cetane-cracking activity.

Zirconium phosphate has been used as a catalyst for the dehydration of alcohols (*38*). However, the catalyst used was not

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well characterized. Since the properties of zirconium phosphate gels are notorious for their dependence upon preparative conditions (*39*), the reported results must be considered to be preliminary and qualitative. More recently an advantageous preparation of methyl isobutyl ketone from acetone was carried out using palladium supported upon a zirconium phosphate gel (*40*). Thus, the acidic properties and uses of zirconium phosphate as a support for dispersed metals presents an interesting system for study since much is now known about this material (*41, 42*). This is especially true since crystalline as well gel forms of zirconium phosphate can be prepared.

Extensive investigations by Clearfield *et al.* (*42–45*) have shown that crystalline α-zirconium phosphate (α-ZrP), α-$Zr(HPO_4)_2 \cdot H_2O$, is an ion exchanger which has a layered structure. The metal atoms lie very nearly in a plane and are sandwiched between two layers of phosphate anions. There are two slightly different monohydrogen phosphate groups in the lattice, termed P_2 and P_3. Horsley *et al.* (*46*) confirmed this fact by means of ir and Raman spectroscopic measurements. Hattori *et al.* (*18*) found that there are two types of acid sites in α-ZrP with remarkably different acid strengths. Furthermore, the acidity was found to increase with the temperature of thermal treatment up to 400°C, beyond which it declines sharply. Nozaki and coworkers (*1*) also observed a similar behavior.

Zirconium phosphate crystallizes slowly from hot phosphoric acid and therefore it is possible to prepare solids with varying degrees of crystallinity ranging from amorphous to large single crystals (*45, 47, 48*). The ion-exchange properties depend upon the degree of crystallinity (*47, 48*) and it is probable that the acidity does also. In addition, several phase changes occur upon heating (*49*). Thus, it is necessary to take all of these factors into account if meaningful relationships between acidity and catalytic behavior are to be uncovered. We report here the acidity and catalytic activity, in dehydration of cyclohexanol, of three samples of α-ZrP which differ in crystallinity.

EXPERIMENTAL

Catalyst preparation. Three separate samples were prepared as described previously (*47*) and labeled 0.5 : 48, 4.5 : 48, and 12 : 336. This designation means that the zirconium phosphate gel was refluxed in 0.5 *M* H_3PO_4 for 48 hr etc. Thus, the first sample is amorphous, the second semicrystalline, and the third highly crystalline. The catalyst samples were characterized by X-ray diffraction, TGA, and BET-surface area.

Acidity measurements. The acidity of these samples was determined by the Benesi method (*27, 28*) using the modification suggested by Bertolacini (*29*). About 200–300 mg of the ZrP catalysts were calcined in special glass cells at the desired temperature for 16 hr. Temperatures of 110, 320, and 400°C were used. The cells were designed with narrow mouths which could be covered with septums immediately after calcination. The cells and contents were then allowed to cool in a desiccator and weighed. In this way, we avoided the possible problem of moisture entering into the cell. About 2 ml of isooctane and 0.1% indicator solution were added through the septum by means of a Hamilton syringe. The cell was then lowered into the water-filled ultrasonic tank. Addition of *n*-butylamine in small stepwise increments was carried out by means of a calibrated syringe. The acid strength is expressed by the Hammett acidity function Ho corresponding to the pK_a value of the indicator. The following indicators were used in the present study.

(1) Methyl Red (pK_a = +4.8)

(2) 4-Benzeneazo-1-naphthylamine (pK_a = +4.0)

(3) Butter Yellow (pK_a = +3.3)

(4) 4-Benzeneazodiphenylamine (pK_a = +1.5)

(5) Dicinnamalacetone (pK_a = −3.0)

(6) Benzalacetophenone (pK_a = −5.6)

Ion exchange with CsCl solution. A known amount of α-ZrP was treated with 50 ml of 0.05 *M* CsCl solution, and the pH of the resulting mixture was noted until a constant value was obtained. The solid was filtered, washed, and dried, and calcined at 400°C for 16 hr. The thermally treated product was again mixed with 50 ml of 0.05 *M* CsCl solution and the equilibrium value of pH was recorded. The Cs^+ exchanged α-ZrP (12 : 336) was tested for its catalytic activity in dehydration of cyclohexanol with a view to determining the poisoning effect of Cs^+ and to find out whether the surface hydroxyl groups played a role in the catalysis. As will be explained subsequently, only the surface protons were exchanged by this procedure (*50*).

Catalytic activity. The reactor system consisted of a U-tube flow reactor (6 mm i.d. and 200 mm height), condensers, and a trap to condense the volatile products coming out of the reactor. The reactor was heated by means of a tubular furnace, the temperature of which was controlled by a Barber Coleman temperature controller. The flow of the reactants was metered with a Sage syringe pump. A known amount of catalyst (~200 mg) was loaded into the reactor and heated in a flow of helium to 350°C for 16 hr; the temperature was then reset to the desired value between 300 and 400°C. Cyclohexanol was introduced after a constant temperature was established. The liquid products were analyzed by using a Hewlett–Packard 5830-A gas chromatograph fitted with an HP 18850 GC terminal; the column was packed with 10% OV-17 on 100/120 Chromosorb WHP. Cyclohexene and water were the only products of the reaction; the amount of cyclohexanone, the dehydrogenation product of cyclohexanol, was less than 0.5%. The gas chromatograph (operating in ESTD and NORM modes) was calibrated by injecting mixtures of cyclohexene, cyclohexanol, and cyclohexanone of known molar composition. In this way, we could directly obtain the percentage molar composition of products from the chromatogram. Since 1 mole of cyclohexanol gives 1 mole of cyclohexene and because the amount of cyclohexanone was found to be negligible (<0.5%), the amount of cyclohexene given in the NORM mode is referred to as the conversion (A). We define the activity (A^*) as the slope of the first order plots in which $[-2 \ln(1 - A) - A]$ vs the contact time t are plotted; A is the conversion and t is defined as the ratio of the weight of catalyst(g) to the feed rate (g/min).

Quinoline titrations were performed in the following way. A pulse of quinoline was injected into the reactor. The fall in conversion (A) with time was noted until a constant value was reached. The effect of pulse size on the conversion (A) at 300, 350, and 400°C was assessed in a similar manner. Contact time was 0.84 min.

Instrumental. X-Ray powder patterns were taken with a Norelco (Philips) wide angle diffractometer at a scan rate of 1° per min using nickel filtered Cu radiation (CuK_α = 1.5418 Å). A Cahn Electrobalance was used for the thermogravimetric analysis. An Orion 801 digital pH meter was used for pH measurements during Cs^+ ion exchange. Surface areas of samples 0.5 : 48 and 12 : 336 were determined by krypton adsorption while that of 4.5 : 48 was determined by nitrogen adsorption using a Micromeritics Digisorb 2500 automatic multigas surface area and pore volume analyzer. The samples were degassed overnight at 250°C.

RESULTS

Thermogravimetric Analysis

Weight loss curves for the zirconium phosphate samples are shown in Fig. 1. The crystalline samples (4.5 : 48 and 12 : 336) lose water in two steps before the transformation from α-phase to the pyrophosphate

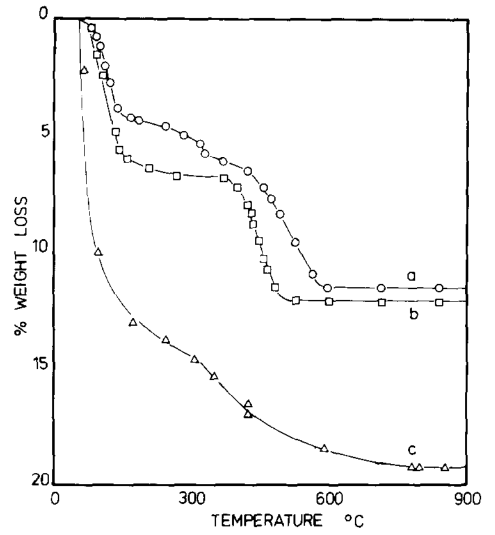

FIG. 1. TGA curves of α-zirconium phosphates used in this study. ○ ZrP (12:336), ☐ ZrP (4.5:48), and / ZrP (0.5:48).

phase occurs, while a continuous loss of water is observed in the case of the amorphous gel (0.5:48) until it condenses into the pyrophosphate form. These results parallel those observed previously (47, 49).

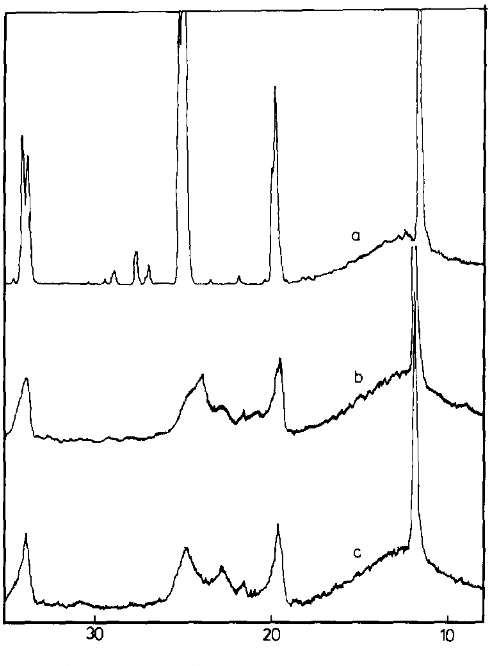

FIG. 2. X-Ray diffraction patterns of α-ZrP. (a) Before heating, (b) after heating at 300°C, and (c) after heating at 400°C.

Phase Changes on Heating

Figure 2 shows the X-ray diffraction patterns of the crystalline samples after they have received various thermal treatments. Upon heating the sample (12:336) to 110°C, its structure changed from α- to ζ-phase and at further heating to 320°C or above to the η-phase which upon cooling yields the ζ-phase even at room temperature. In some cases, when heating is prolonged at 400°C and the sample cooled rapidly, some η-ZrP was found to constitute part of the solid at room temperature. These findings are in conformity with previously reported data (*49*).

Surface Area Measurements

The surface areas of the catalysts under investigation are summarized below:

Sample	Surface area (m^2/g)(BET)
ZrP 0.5:48	2.7
ZrP 4.5:48	34.6
ZrP 12:336	1.8

Acidity Measurements

Acid strength distributions for the zirconium phosphate samples pretreated at 110, 320, and 400°C are presented in Fig. 3. The amount of acid determined with an indicator of $pK_a = +4.8$ was found to be about 6.2 ~ 6.3 mequiv/g for samples ZrP (4.5:48) and (12:336) at all three temperatures. This is very close to the theoretical exchange capacity of α-ZrP and indicates that the measured acidity is due to the monohydrogen phosphate groups. The two crystalline samples when preheated to 110°C exhibited about the same acid group distribution, viz. 5.75–5.8 mequiv/g with $pK_a + 4.8 \geq \text{Ho} \geq +3.3$, 0.05–0.08 mequiv/g with $pK_a + 3.3 \geq \text{Ho} \geq -3.0$, and 0.35 mequiv/g with $pK_a - 3.0 \geq \text{Ho} \geq -5.6$. With increasing temperature of pretreatment the total amount of

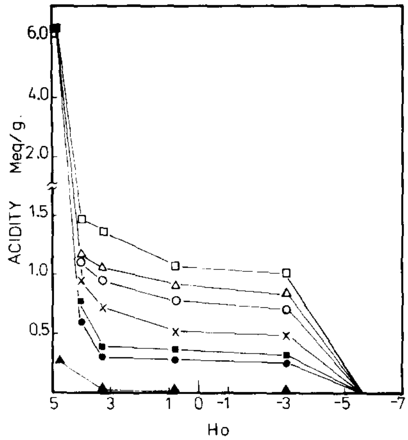

FIG. 3. Acid-strength distribution of hydroxyl groups in α-ZrP heated at various temperatures.

Temperature	ZrP(12 : 336)	ZrP(4.5 : 48)	ZrP(0.5 : 48)
110	●	■	—
320	×	△	—
400	⊙	□	▲

acidity remains constant but the distribution changes. A marked increase in the amount of strong acid groups takes place while a more modest increase in acid groups with $pK_a + 4 \geq Ho \geq +1$ is observed. A similar result has also been observed by Hattori and co-workers for an α-ZrP sample 10 : 48 (*18*). In the case of the amorphous sample 0.5 : 48, almost all of the acid groups were destroyed by heating at 400°C. It is known that condensation of hydroxyl groups begins at about 180°C in amorphous zirconium phosphate (*51*). The heated sample 0.5 : 48 lost 17.03% water at 400°C (8 hr hold time) and a further weight loss of 2.09% to 900°C. This latter condensation loss corresponds to about $\frac{1}{3}$ of the total hydroxyl content of the original sample (6.62 mequiv/g theoretical for α-ZrP). Thus, about $\frac{2}{3}$ of the hydroxyls were destroyed at 400°C.

Catalytic Activity

The conversion of cyclohexanol to cyclohexene at different temperatures as a function of the contact time *t* in minutes for 12 : 336 is plotted in Fig. 4. A first order rate equation was found to fit the data (Fig. 5). The slope of the straight lines yields the value of the specific reaction rate constant *k* (min^{-1}). Figure 6 shows an Arrhenius plot of ln *k* against the reciprocal of temperature which yields an activation energy of 11.5 kcal/mole. The activity (A^*) of the three ZrP samples, 4.5 : 48 and 12 : 336, at 400°C is compared in Fig. 7 and shows the following trend, A^* (4.5 : 48) > (12 : 336) > (0.5 : 48).

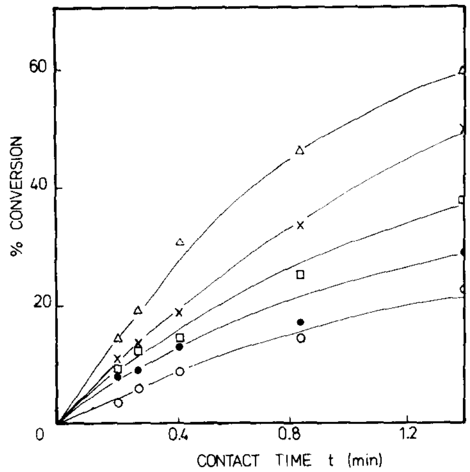

FIG. 4. Cyclohexanol dehydration activity of ZrP(12 : 336) at: ⊙ 300°C, ● 325°C, □ 350°C, × 375°C, and △ 400°C.

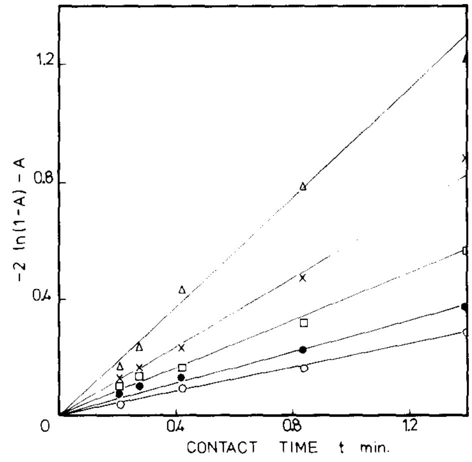

FIG. 5. First order plot of data in Fig. 4 (same symbols).

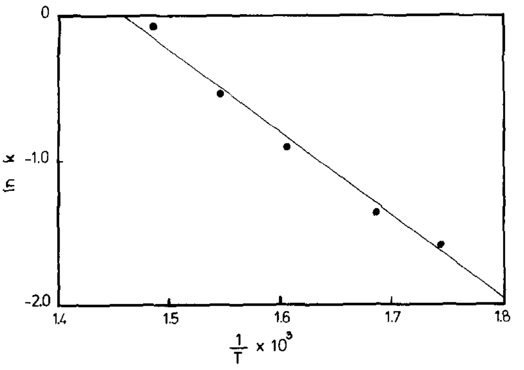

FIG. 6. Arrhenius plot of ln k versus $1/T$ for data of Fig. 5.

Alberti *et al.* have shown that it is possible to exchange only the surface protons of α-ZrP with Cs^+ (*50*). This ion is too large to exchange into the interior of α-ZrP in acid solution (*43*). The total number of protons released by the exchange reaction can be calculated from the pH values at equilibrium and this gives the number of hydroxyl groups covered by Cs^+. It is found that much more protons are released by 4.5 : 48 than 12 : 336 in accord with their different surface areas.

Figure 8 gives the activity (A) for cesium exchanged α-ZrP samples, from which it is seen that Cs^+ ion exchange inhibits the reaction considerably.

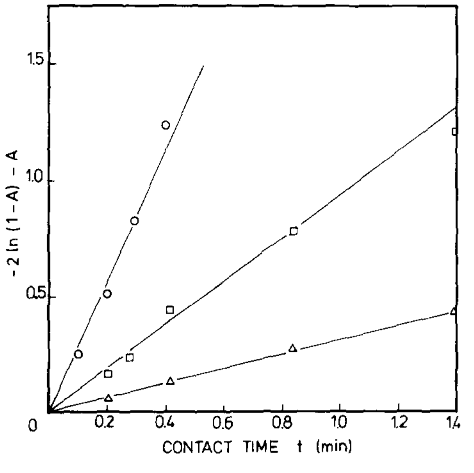

FIG. 7. A comparison of activities (A^*) at 400°C. ⊙ ZrP(4.5 : 48), k = 2.75.; □ ZrP(12 : 336), k = 0.932; △ ZrP(0.5 : 48), k = 0.324.

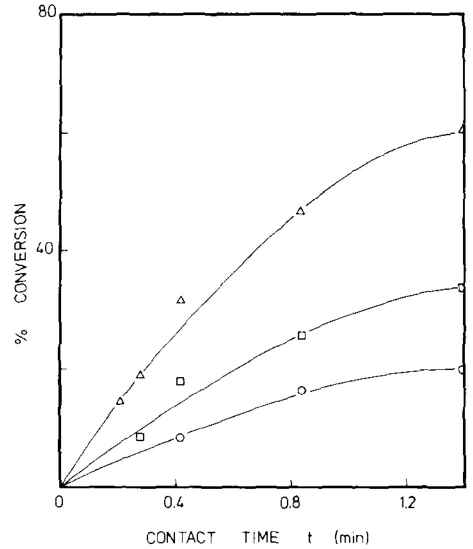

FIG. 8. Effect of Cs^+ ion exchange on the activity (A) of α-ZrP(12 : 336). α-ZrP(12 : 336) no Cs^+ exchange, △; after first treatment with CsCl, □; after second treatment with CsCl, ○.

Quinoline titrations performed at 300, 350, and 400°C are shown in Fig. 9; each point represents the steady-state conver-

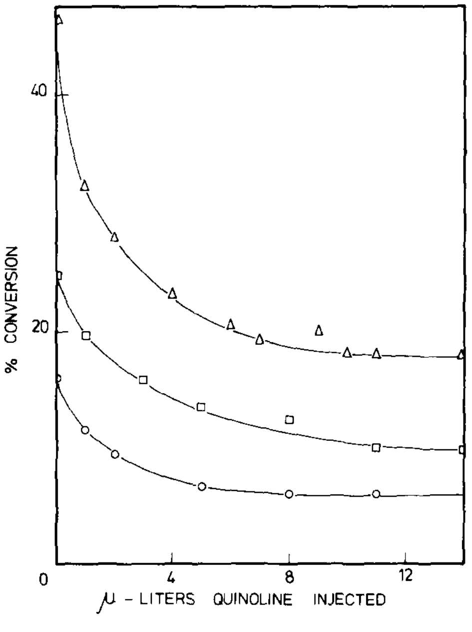

FIG. 9. Effect of quinoline on dehydration of cyclohexanol by α-ZrP(12 : 336); W/F = 0.84 min; △, 400°C; □, 350°C; ⊙, 300°C.

sion obtained (at contact time $t = 0.84$ min) by injecting a known amount of quinoline. The conversion decreased from 46 to 18% at 400°C, from 25 to 10% at 350°C, and from 16 to about 5–6% at 300°C.

DISCUSSION

The TGA and X-ray diffraction patterns of ZrP (12:336), shown as curve a in Figs. 1 and 2, correspond to a highly crystalline α-ZrP phase as defined by Clearfield and Pack (*49*) and Horsley *et al.* (*46*). Thermal treatment of this sample at temperatures ranging from 110 to 400°C results in a loss of 1 mole of water (Fig. 1a) as well as a series of phase transformations from α- to ζ- to η-ZrP. These findings are in accordance with those of Clearfield and Pack (*49*). The latter transformation occurs at about 230°C so that most likely the reactions were carried out on this phase. The amorphous gel, however, undergoes a substantial condensation of phosphate groups at 400°C, leading to the formation of pyrophosphate. Hattori *et al.* (*18*) in their investigations on a less crystalline sample ZrP (10:48) report similar phase transformations upon thermal treatment.

Let us now consider the acidity measurements shown in Fig. 3, which indicate that the total amount of acid groups, as determined by butylamine titration, remains constant at 6.2 ~ 6.3 mequiv/g independent of the heat treatment of the sample. This value is nearly but not quite the exchange capacity of α-ZrP (*43*). The difference may result from the difficulty in intercalating the stoichiometric amount of amine in between the layers (*52*). Figure 3 also shows that the amount of acid with $+3.3 \geq \text{Ho} \geq -3.0$, which is practically constant at a given temperature, is a function of the temperature of thermal treatment in the sense that it increases with increase in temperature. These findings correspond fairly well with those of Hattori *et al.* (*18*) who used a sample of α-ZrP, 10:48.

This increase in the amount of acid in the range of $+3.3 \geq \text{Ho} \geq -3.0$ indicates that strong acid sites are generated on heating the sample from 110 to 400°C. The fact that the total amount of acid remains constant at 6.2–6.3 mequiv/g suggests that the increase in strong acid sites is probably counterbalanced by a decrease in weak sites. It, thus, follows that the weak acid sites are converted to stronger sites by the thermal treatment. Hattori *et al.* (*18*) have shown by ir spectroscopy that the weak as well as the strong acid sites are due to the POH groups. In catalysis studies the term acidity, as commonly used, refers to the surface acidity or to those sites available to the reactant molecules. The number of surface hydroxyl groups in α-zirconium phosphate can readily be calculated from measured surface areas and/or the number of protons liberated by surface exchange. Each hydroxyl group occupies 23.99 Å^2 in α-ZrP (*53*). Thus, sample 12:336 contains 7.5×10^{18} hydroxyls/g or 0.012 mequiv/g. This is far less than the number of strong acid groups determined by butylamine titration. The same is true for sample 4.5:48. However, X-ray diffraction patterns of the titrated samples, taken at the point (Fig. 3) where Ho = −3, revealed the presence of two phases. One is the original ζ-ZrP phase and the other a phase with a 10.5 Å interlayer spacing. This latter phase is a butylamine intercalate in which it is thought that the amine groups lie parallel to the layers (*52*). Even the α-ZrP phase may contain some amine in the interior since it has been shown in aqueous solutions that initially some amine is intercalated into α-ZrP without phase change (*52*). Thus, the major portion of the strong acid groups, as determined by butylamine titration, lies in the interior of the solid where they are largely inaccessible to the cyclohexanol molecules. The further large uptake of amine at Ho greater than +3 results in the conversion of the solid to a phase with interlayer spacing of 18.2 Å. In this phase the amine forms a bilayer (*52*) similar to that in clays.

In a separate experiment 0.5 g of 12:336 was shaken with a 0.05 *M* solution of CsCl and found to liberate 0.005 mequiv of H^+ or 0.01 mequiv/g. This corresponds to 0.6×10^{19} protons and a surface area of 1.44 m^2/g in good agreement with the value from N_2 adsorption. With α-ZrP(4.5 : 48) the uptake was higher than that of ZrP(12 : 336) and corresponds to 8.3×10^{19} surface protons/g or a surface area of 20 m^2/g compared to a measured value of 34.6 by BET nitrogen adsorption. The difference between these two samples, ZrP(4.5 : 48) and ZrP(12 : 336), arises essentially from the difference in their crystallinity, the former being refluxed in weaker acid-formed smaller particles and hence has more surface area, thus more –OH groups on the surface relative to the interior.

The catalytic activity data (Fig. 4) show that zirconium phosphate is extremely selective toward the dehydration reaction; dehydrogenation of cyclohexanol to cyclohexanone is found to be less than 0.5%. It must also be pointed out that we did not observe any other side reaction (series reaction) of isomerization of cyclohexene to methylcyclopentenes like the one described by Sharf *et al.* (*54*) on zirconium phosphate. Very strong acid sites are normally involved in such a reaction (*55*), which are present on some alumina surfaces. Our results indicate that these sites are not present on ZrP.

Among the several empirical equations developed by assuming different values of the order of reaction from 0 to 2 (*56*), only the first-order rate expression

$$-2 \ln(1 - A) - A = kt \qquad (1)$$

was found to fit the data adequately. Although, the dehydration of alcohols over various catalysts has been reported to follow zero-order kinetics (*1*, *2*), an increase in reaction order from 0 below 125°C to 1 at 200°C in zeolite catalyzed alcohol dehydration is found consistent with a Langmuir–Hinshelwood mechanism (*57*). A plot of $[-2 ln(1 - A) - A]$ against the contact time t yields a straight line with a slope equal to k—the specific reaction rate constant (Fig. 5). The activation energy calculated from the plot of ln k against the reciprocal of temperature T(°K) was found to be 11.5 kcal/mol (Fig. 6) for 12 : 336. This corresponds fairly well with the value, 9.1 kcal/mol, reported by Nozaki *et al.* (*1*) for 2-propanol dehydration on ZrP at temperatures above 230°C.

A comparison of the activities (A^*) of various samples (Fig. 7) shows that ZrP(4.5 : 48) is about 3 times more active than ZrP(12 : 336), and about 9 times greater than ZrP(0.5 : 48). We feel that the difference in their activities is related to their surface areas and to their structural properties at elevated temperatures which together determine the number of strong acid groups. Preliminary results (*58*) indicate that the activities of different ZrP samples can be correlated with the number of surface hydroxyl groups as determined by ammonium ion uptake (*53*). The very low activity of 0.5 : 48 is attributed to the fact that most of its hydroxyl groups are condensed out as water at 400°C.

If the surface hydroxyl groups were solely responsible for the dehydration activity replacement of the protons by Cs^+ should eliminate this activity. A sample of catalyst 12 : 336 which had been treated with 0.05 M CsCl indeed showed diminished activity (Fig. 8). Its rate constant was 0.344 min^{-1} and is very close to that for sample 0.5 : 48 (0.324). A second treatment with 0.05 M CsCl yielded a still lower rate constant of 0.22 min^{-1}.

The extent of influence exerted by quinoline on the conversion is clearly demonstrated in Fig. 9, in which the steady-state conversion is plotted against the amount of quinoline, at different temperatures. The conversion decreases rapidly in the beginning and then levels off at all temperatures studied. These results are quite similar to those observed by Goldstein and Morgan (*35*) and Topchieva *et al.* (*32–34*), who studied the poisoning effects of quinoline on the cumene-cracking activity of zeolites. Topchieva *et al.* (*32*) observed that addition of quinoline beyond 0.09 mmol/g did not change the cracking activity of zeolites. On the basis of their results with quinoline titrations and alkali metal exchange experiments, they proposed the existence of two types of active centers.

Although one can correlate the higher activity exhibited by the semicrystalline ZrP(4.5 : 48) to its acidity, one cannot explain the activity of the anhydrous gel (0.5 : 48) in terms of its acidity, which is practically negligible at 400°C. The activity of the latter is comparable to that of Cs^+ ion-exchanged ZrP(12 : 336) after first treatment. Although, the poisoning experiments (Figs. 8 and 9) suggest the participation of protons in the chemical reaction the fact that the catalyst does not get totally poisoned indicates that the catalytic activity of zirconium phosphates is governed not only by the number of protons (or acid strength) but also by certain unknown inherent characteristics or surface defects created by structural modifications at elevated temperature. In other words, the present observations suggest the presence of at least two kinds of sites on zirconium phosphate perhaps like those in zeolites (*32*). One of the sites, which gets poisoned by quinoline or Cs^+ ion exchange, should be related to the hydroxyl group (Bronsted acid site). It should be mentioned here that the decrease in activity brought about by quinoline poisoning (initial 46% to final 18%) and that by Cs^+ ion exchange (initial 46% to final 17%) at $W/F = 0.84$ min is quite comparable and hence we feel that poisoning of the same kind of sites is responsible for this fall in activity. The residual activity in both the cases (18 and 17%) is nearly the same as the activity of the amorphous gel ZrP(0.5 : 48) in which most of hydroxyl groups condense at 400°C. This fact leads us to assume that the second kind of site which does not get poisoned by quinoline or Cs^+ ion or by thermal treatment should be responsible for the residual activity of ZrP(12 : 336) and for the activity of amorphous ZrP gel (0.5 : 48). This second kind of site should be associated either with the phase–phase transformation from α- to ζ-ZrP (or η-ZrP) or to a zirconium–oxygen bond stretching or Lewis-type centers formed by removal of protons. A detailed structural analysis of ζ- and η-ZrP phases would help to explain the activity of zirconium phosphate catalysts.

Another point to note is that the turnover numbers obtained from the rate constants at 400°C are ~12 molecules/sec per hydroxyl group for 12 : 336 but only 2 for 4.5 : 48. Thus, the improved conversion rates of 4.5 : 48 are due in large measure to the fact that it contains so many more hydroxyls than 12 : 336. Experiments designed to uncover the reasons for this difference in reactivity of the hydroxyl groups are in progress.

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