Cyclohexanol Dehydration over Zirconium Phosphates of Varying Crystallinity

The decomposition of alcohols is a widely used test reaction for acidic catalysts (*1–3*). Excellent reviews concerning the mechanism of dehydration of alkanols over various catalysts have been published (*4–6*). Extensive work has been done to elucidate the nature of active sites (*7–15*) and there appears to be some correlation with the relationship between catalytic activity (in dehydration and dehydrogenation of alcohols) and the strength of acidic or basic sites of the catalysts.

Metal phosphates have been extensively studied as dehydration catalysts during the last few years (*1, 6, 8, 12, 15*). Earlier work from this laboratory (*16*) showed that crystalline zirconium phosphate, $Zr(HPO_4)_2$, selectively catalyzes the dehydration of cyclohexanol to cyclohexene. Although we could not arrive at a definite correlation between catalytic activity and acidic strength, poisoning experiments (with quinoline and Cs^+ ion) showed the presence of at least two kinds of sites on zirconium phosphates (hereinafter called α-ZrP). The more important catalytic site is that associated with the protons of the surface P–OH groups. The second site is probably of the Lewis acid type associated with the zirconium atoms or with defects caused by hydrolysis of HPO_4^{2-} groups.

In the present note, we shall correlate the dehydration activity of a series of zirconium phosphate samples with their effective surface area, i.e., the number of surface hydroxyl groups.

EXPERIMENTAL PROCEDURE

Catalyst preparation. A series of zirconium phosphate samples with different crystallinities was prepared by the method described by Clearfield *et al.* (*17*). These samples are labeled as ZrP 2.5 : 48, 3.5 : 48, 4.5 : 48, 6 : 48, 9 : 48, 12 : 50, 12 : 100, and 12 : 336, where the first number represents the molar concentration of H_3PO_4 acid and the second number, the duration of reflux in hours. It was shown previously that the crystallinity increases with time of refluxing and concentration of acid (*17*).

Surface area determination. An earlier study showed that NH_4^+ solutions at acid pH values exchange only surface protons from α-ZrP if the crystallinity of the exchanger is not too low (*18, 19*). Thus, exhaustive treatment of the exchanger with NH_4Cl liberates all (or nearly all) of the surface protons. Since each P–OH group occupies 23.99 $Å^2$ of surface, the surface area is readily calculated from the number of protons liberated. Ammonium ion exchange of the surface was carried out as before (*18*) with the difference that the solid and solution were separated by centrifugation and the supernatent solutions combined and titrated with standard base to pH 5. At this pH essentially all of the protons are neutralized but not the solubilized phosphate groups. BET surface areas were determined by N_2 adsorption in the usual way.

Catalytic activity. The catalytic activity was determined at 350°C in a continuous-flow reactor on α-ZrP samples pretreated as described elsewhere (*16*). The flow rate was varied by injecting the alcohol with a Sage syringe pump into a stream of helium at different rates. The total volume of gaseous alcohol was such that its pressure varied from 0.78 atm at the slowest flow to 0.90

atm at the fastest. No correction for this variation in pressure was made. Each run consisted of exactly a 5-ml injection of alcohol. The total product mix was collected, weighed for mass balance, and analyzed by means of gas chromatography. In all cases less than 0.5% of cyclohexanone was obtained and no methylcyclopentenes. Mass recovery was of the order of 98–99%. Catalyst poisoning experiments were carried out both with quinoline and by exchanging out surface protons with Cs^+.

RESULTS AND DISCUSSION

Figure 1 shows the variation of cyclohexanol dehydration activity with contact time for zirconium phosphate samples of different crystallinities. As expected, the rate of cyclohexanol dehydration to cyclohexene increases as one goes from crystalline α-ZrP 12:336 (low surface area) to semicrystalline α-ZrP 2.5:48 (high surface area). The activity of the amorphous gel, ZrP 0.5:48, was found to be considerably lower than those of the other samples (α-ZrP 2.5:48 to 12:336) because of an appreciable condensation of its phosphate groups at the reaction temperature (16). The dehydrogenation of cyclohexanol to cyclohexanone for these samples was less than 0.5%.

It has been shown previously that the degree of crystallinity of zirconium phosphates depends upon the concentration of
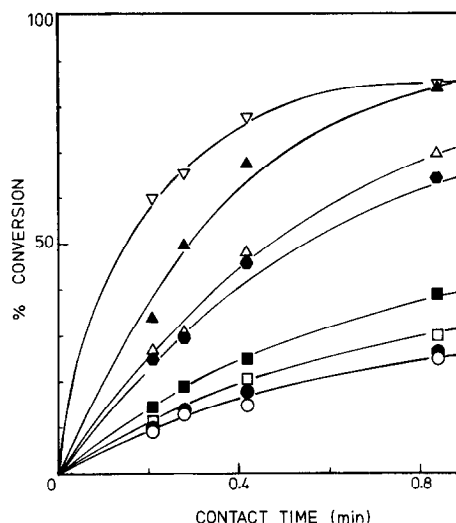

FIG. 1. Cyclohexanol dehydration activity of ZrP samples of varying crystallinity. (T = 350°C). ZrP 2.5:48, ▽; ZrP 3.5:48, ▲; ZrP 4.5:48, △; ZrP 6:48, ◕; ZrP 9:48, ■; ZrP 12:50, □; ZrP 12:100, ●; ZrP 12:336, ○.

phosphoric acid and the reflux time (17, 20); weaker phosphoric acid solutions and shorter time intervals give smaller crystallites (2.5:48, etc.), while the stronger acid concentration and prolonged refluxing treatment result in the formation of larger crystallites (12:336). The data in Table 1 show that surface areas depend upon the degree of crystallinity. Surface areas determined by NH_4^+ exchange are somewhat low as compared to BET values indicative

TABLE I

Influence of Surface Protons on the Specific Rate Constant of Cyclohexanol Dehydration

Catalyst	Total NH_4^+ uptake (Meq/g)	Surface area (m²/g)		Specific rate constant (min⁻¹)
		NH_4^+ exchange	BET	
2.5:48	0.498	72.0	90	5.51
3.5:48	0.440	64.0	—	3.70
4.5:48	0.180	26.0	34.6	2.13
6.0:48	0.135	20.0	—	1.81
9.0:48	0.054	7.8	7.8	0.70
12:50	0.038	5.5	—	0.52
12:100	0.022	3.2	—	0.40
12:336	0.021	3.0	1.8	0.40

of incomplete exchange or hydrolysis of some surface phosphate groups.

The increase in catalytic activity with increase in surface area leads to the conclusion that the activity depends upon the number of surface protons. It was found earlier that the rate of cyclohexanol dehydration follows first-order kinetics (16). Rate constants for various catalysts were evaluated by using the expression

$$-2\ln(1 - x) - x = kt,$$

where x is fractional conversion, k is the specific rate constant, and t is contact time which is a ratio of weight of catalyst (g)/flow rate (g/min).

In homogeneous acid–base catalysis, the rate constant of a reaction is related to the acid strength of the catalyst by the Brönsted relation (20). In heterogeneous reactions Jerabek et al. (11) have shown the dependence of the specific rate constant for tert.-butanol dehydration on the acid strength of the acidic solid catalysts. Acid strengths for zirconium phosphate have been measured by the Benesi method (16, 22). Zirconium phosphate is an ion exchanger and has a layer structure in which zirconium atoms lie nearly in a plane and are bridged by monohydrogen phosphate groups (21). Titration with butylamine results in intercalation of one butylamine molecule for every monohydrogen phosphate group, i.e., the theoretical exchange capacity of 6.64 meq/g. Thus, we assume that the butylamine is reacting only with the P–OH groups. These groups fell into one of two types, either strong or weak (only a small number were of intermediate acidity) (16). The number of weak acid groups was very large compared to the number of strong acid groups and must in the main represent hydroxyls in the interior of the zirconium phosphate. The number of strong acid groups far outnumbers the total number of surface hydroxyl groups. Thus, we assume that all the surface P–OH groups (together with some in the interior) are strong and of approximately the same

strength. A plot of log k, the specific rate constant for cyclohexanol dehydration, versus the log of the number of surface hydroxyl groups, as measured by ammonium ion exchange, is shown in Fig. 2. A straight line relationship is obtained which however deviates at low values of log[OH]. The plot tends to become asymptotic to the ordinate indicating very little change in activity with decrease in the number of surface hydroxyl groups beyond a certain point. In this context, it should be remarked here that catalyst poisoning experiments had shown the presence of two kinds of sites on ZrP samples (16). One of these sites is poisoned by quinoline or Cs^+ ion exchange and hence should be related to surface hydroxyl groups, while the other one contributes to the residual activity of semicrystalline and crystalline ZrP samples, or to the activity of the amorphous ZrP gel (0.5:48) in which nearly complete dehydroxylation was effected by pretreating the sample. The nature of the latter type of site is not clearly understood as yet but it may be of the Lewis acid type. The present results, coupled with those obtained earlier (16), suggest that their participation in the catalysis of cyclohexanol dehydration is responsible for the residual activity and
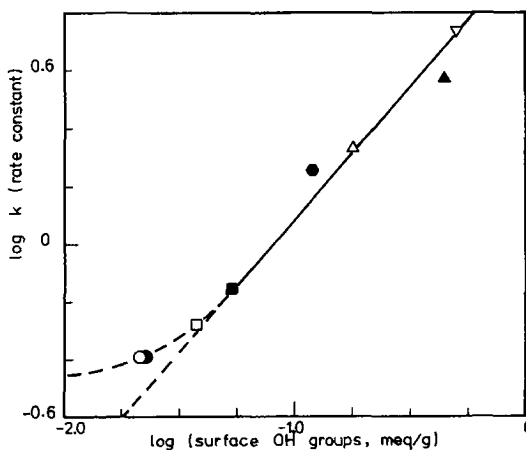

FIG. 2. Logarithmic plot of specific rate constant against number of surface hydroxyl groups of various ZrP samples. Symbols are the same as those in Fig. 1.

hence for the deviation from the linear dependence of k on the number of surface –OH groups in the lower portion of Fig. 2. Recently, Malinowski and Tyblewski (12) have reported that the Lewis acid sites, formed during the calcination of nickel phosphate catalyst at elevated temperatures, play a predominant role in isopropanol dehydration. Their conclusion is based on the fact that the catalysts heat-treated at temperatures higher than 700°C, although practically devoid of –OH groups, exhibit appreciable activity in isopropanol dehydration. Our catalysts were heated to 400°C but even this temperature may be sufficient to create some Lewis acid sites since some condensation of monohydrogen phosphate groups was found to occur at this temperature in 24 hr.

The slope of the straight line plot (Fig. 2) is about 1, which indicates that at surface areas of 5–6 m²/g and higher there is a direct correspondence between the rate constant and the number of surface hydroxyl groups. Turnover numbers, molecules of cyclohexanol converted per second per hydroxyl group, are relatively constant (2.2 ± 0.1 for samples 12:50, 9:48, and 6:48; 1.7 ± 0.2 for 4.5:48, 3.5:48, and 2.5:48) over the straight line portion but increase to 3.2 for the two lowest-surface-area samples. We feel that this is due to a relatively fixed contribution from the second nonhydroxyl kind of site. This site most likely plays a more important role for the highly crystalline samples than for the semicrystalline ones, because of the larger number of these sites relative to the number of hydroxyl groups. The higher overall rates for the semicrystalline samples are then due to their much larger surface hydroxyl content.

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