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Basic Properties of Metal Phosphates and Their Catalytic Activity in the Decomposition of Diacetone Alcohol

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The basic properties of alkali and alkaline earth metal phosphates calcined at various temperatures were investigated. The strength of the surface base was determined by the adsorption of acidic indicators from benzene solution. It was found that K_3PO_4 shows a fairly high basic strength of $H_0 \geqq 17.2$. The surface basicity was evaluated by the catalytic activity for the decomposition of diacetone alcohol, which is known to be catalyzed only by basic catalysts. Comparison of the result of the activity measurement with that of TGA indicated that the basicity of a metal phosphate reaches a maximum when dehydrated completely. The nature of the basic sites on metal phosphates is also discussed.

The surface basicities of metal phosphates have not been extensively studied as compared to the surface acidities of those. Scheidt[1)] has reported that lithium phosphate, sodium orthophosphate, and calcium orthophosphate catalyze aldol condensations which are typically base-catalyzed. On the other hand, the condensation of acetaldehyde in low yield by passing the feed in the vapor phase over magnesium, zinc, strontium, cadmium, or barium phosphates has been reported by Ivanov *et al.*[2)] In our preceding paper,[3)] the surface of sodium and calcium orthophosphates was found to have a basic character, but that of others such as magnesium, zinc, or nickel salts an acidic character. These observations seem to be in agreement with the above results. Recently, Imanaka *et al.*[4)] have reported that Li_3PO_4 has only acidic character, but Li_2MPO_4- and LiM_2PO_4- type phosphates (M=Na or K) and $Ca_3(PO_4)_2$ have both basic and acidic properties. The basic properties of metal phosphates are considered to be closely related to their structures, and it is important to clarify the relations between them. Very little work, however, has been made on such relationships. From these point of view, an attempt was made to clarify the nature or structure of the basic sites on metal phosphates calcined at various temperatures.

Experimental

Samples. The following chemicals were reagent grade, and were used without further treatment: $Ca_3(PO_4)_2$, $Na_3PO_4 \cdot 12H_2O$, K_3PO_4, Li_3PO_4, $Na_2HPO_4 \cdot 12H_2O$, $NaH_2PO_4 \cdot 2H_2O$, $Ca(H_2PO_4)_2 \cdot H_2O$, K_2HPO_4, KH_2PO_4, and $Na_4P_2O_7 \cdot 10H_2O$. $Na_2HPO_4 \cdot 12H_2O$ and $Na_3PO_4 \cdot 12H_2O$ were first calcined at about 130 °C for 6—7 hr, sieved below 100 mesh after grinding to powder and then calcined at various temperatures for 3 hr in air. The other phosphates were calcined immediately after sieving.

Measurement of Basic Property. The basicities and basic strengths of samples were measured by titrating the powder suspended in benzene with 0.1 N benzoic acid benzene solution, using bromothymol blue ($pK_a = 7.1$), phenolphthalein (9.3), 2,4-dinitroaniline (15.0), and 4-chloro-2-nitroaniline (17.2) as indicators.

Measurement of Catalytic Activity. Decomposition of diacetone alcohol, which was selected as a model reaction, was carried out in the temperature range 30—55 °C, by stirring the reaction mixture in a reaction vessel containing 1.0 g of catalysts, 23.0 g of diacetone alcohol, and 2.5 g of benzene (internal standard). At an appropriate time interval, stirring was stopped and 0.15 ml of the solution was taken up through sampling rubber and analyzed by gas chromatography, after the catalyst had been removed by centrifuging. Diacetone alcohol was purified by drying with Drierite and distilling two times under 10 Torrr.

TGA and DTA. The rate of heating was maintained at 5 °C/min. The sample holder was a platinum vessel.

Results and Discussion

Basic Property. The basic color of the indicator adsorbed on the solids changes to acidic color on addition of benzoic acid but the acidic color changes again gradually to the basic color after several minutes. The results of the basic strength measurements, given in Table 1, suggests that the tertiary phosphates of sodium, potassium, and calcium as well as the secondary phosphates of sodium and potassium may be used as solid base catalysts. The basic strength of tertiary potassium phosphate is comparable to that of an alkaline earth metal oxide.[5)] Although secondary potassium phosphate might show catalytic activity, its effectiveness is probably limited. Lithium phosphate is known to be a catalyst for aldol condendsation reaction,[1)] but Li_3PO_4 shows no solid basicity in agreement with the result of Imanaka *et al.*[4)] This fact suggests that the lithium phosphate used by Scheidt is not Li_3PO_4 but

TABLE 1. BASIC STRENGTH OF ALKALI AND ALKALINE EARTH METAL PHOSPHATES

Original metal phosphate	Calcination temp., °C	Basic strength (H_0)[a)] 7.1	9.3	15.0	17.2
Li_3PO_4	22—400	−	−	−	−
$Na_3PO_4 \cdot 12H_2O$	22—700	+	+	−	−
$Na_2HPO_4 \cdot 12H_2O$	22— 60	−	−	−	−
	150—500	+	+	−	−
$NaH_2PO_4 \cdot 2H_2O$	22—400	−	−	−	−
$Na_4P_2O_7 \cdot 10H_2O$	22—500	−	−	−	−
K_3PO_4	22—800	+	+	+	+
K_2HPO_4	22—500	+	−	−	−
KH_2PO_4	22—400	−	−	−	−
$Ca_3(PO_4)_2$	22—600	+	+	−	−
$Ca(H_2PO_4)_2 \cdot H_2O$	22—400	−	−	−	−

a) + or − denotes yes or no.

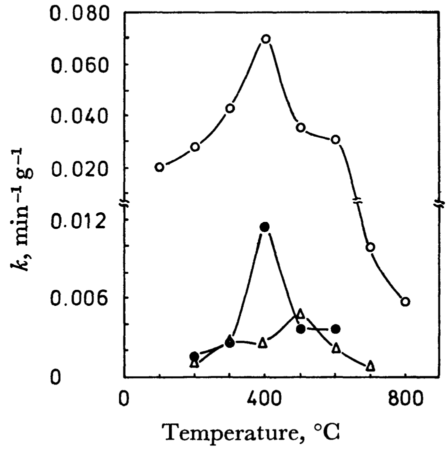


Fig. 1. The reaction rate constants over phosphates at 40 °C as a function of the calcination tempetraure.
○: K_3PO_4, ●: $Ca_3(PO_4)_2$, △: Na_3PO_4

a substituted phosphate such as $NaLi_2PO_4$. $Ca_3(PO_4)_2$ has been found to have both acidity (H_0=4.8) and basicity (7.1).[4] According to Table 1, this salt has only basicity (9.3). This inconsistency may be due to a difference in the samples.

Decomposition of Diacetone Alcohol. The only reaction product was acetone. It has been observed that the rate of decomposition of diacetone alcohol catalyzed by $MgO–Al_2O_3$[6] and alkaline earth metal oxides[7] is of the first order. Similarly the rate on the metal phosphates was found to be of the first order with respect to diacetone alcohol concentration. Fukuda *et al.*[7] have reported that a long induction period is observed on SrO and BaO, while it disappears by the removal of CO_2. However, no induction period was observed on the metal phosphates. The reaction rate constants over the tertiary phosphates of potassium, sodium, and calcium at 40 °C as a function of the calcination temperature are shown in Fig. 1. The catalytic activity of secondary sodium phosphate was much lower under similar conditions. Since the decomposition of diacetone alcohol is known to be catalyzed only by basic catalyst,[7] the catalytic activity is considered to be proportional to the amount of effective basic sites. Only tertiary potassium phosphate showed the catalytic activity at 30 °C. At 40 °C tertiary sodium phosphate, secondary sodium phosphate, and tertiary calcium phosphate were also found to be active, but secondary potassium phosphate inactive. These observations show that the effective basic sites at 40 °C are those having a basic strength of $H_0 \geqq 9.3$.

Table 2. Activation energies of decomposition of diacetone alcohol with various catalysts

Catalyst	Calcination temp., °C	Activation energy[a)] (kcal/mol)
Na_3PO_4	500	10.8
K_3PO_4	400	21.7
$Ca_3(PO_4)_2$	400	18.0
MgO	500	11.1
CaO	500	11.5
SrO	500	20.3
BaO	no heat treatment	20.3
NaOH (aq. soln.)		18.4

a) Activation energies for catalysts from MgO to NaOH are cited from Ref. 7.

Arrhenius activation energies in the temperature range from 30 to 55 °C are compared to the literature values in Table 2. The activation energy for tertiary sodium phosphate is comparable with those for CaO and MgO, while the activation energies for other phosphates are comparable with those for SrO, BaO, and NaOH solution. The activation energy for tertiary potassium phosphate is considered to be rather high in view of its basic strength of $H_0 \geqq 17.2$. This may be related to the formation of light brown, unknown substance on the catalyst during the reaction.

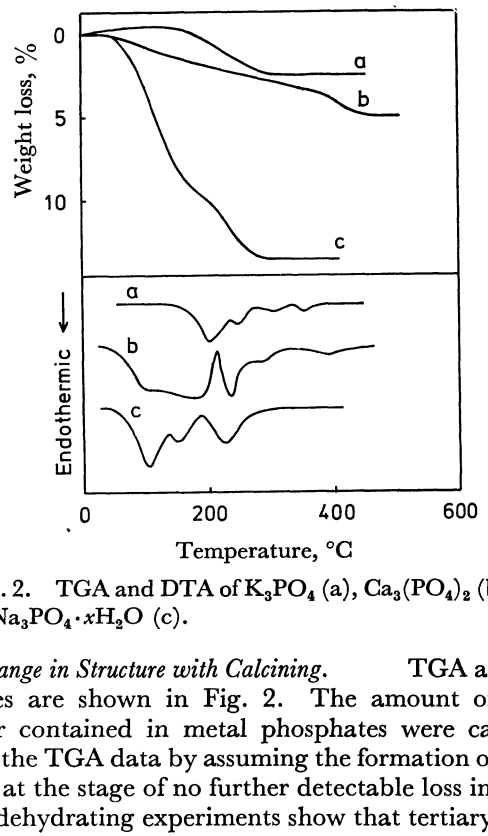
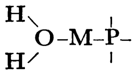


Fig. 2. TGA and DTA of K_3PO_4 (a), $Ca_3(PO_4)_2$ (b), and $Na_3PO_4 \cdot xH_2O$ (c).

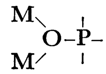
Change in Structure with Calcining. TGA and DTA curves are shown in Fig. 2. The amount of crystal water contained in metal phosphates were calculated from the TGA data by assuming the formation of anhydrides at the stage of no further detectable loss in weight. The dehydrating experiments show that tertiary sodium phosphate predried at 130 °C contains about 1.5 mol of water. The anhydride formation is detected at about 250 °C in agreement with the literature value.[8] The initial increase in weight of tertiary potassium phosphate may be attributable to the absorption of moisture during weighing, because this substance is highly hygroscopic. The water is lost at 280 °C in agreement with the result of Ben-Dor and Felner.[9] According to Fig. 2, it is obvious that $Ca_3(PO_4)_2$ contains about 1 mol of water and reaches complete dehydration at 400 °C. $Na_2HPO_4 \cdot 12H_2O$ has been reported to lose its water of hydration when heated up to 110 °C, and at 300 °C condensation to the pyrophosphate occurs.[9]

Basic Sites on Metal Phosphates. The structures of metal phosphates have been studied by many workers.[10] In hydrated metal orthophosphates, the phosphorus atoms are tetrahedrally surrounded by oxygen atoms, and the metal atoms (M) are surrounded by the oxygens of the PO_4 groups and of the water molecules, while in anhydrous metal phosphates, the metal atoms are surrounded only by the oxygens of the PO_4 groups. Thus, the following structures I and II are considered



$\mathrm{H_2}\!\!>\!\mathrm{O{-}M{-}\overset{|}{\underset{|}{P}}{-}}$

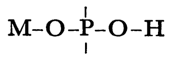
I



$\mathrm{M_2}\!\!>\!\mathrm{O{-}\overset{|}{\underset{|}{P}}{-}}$

II

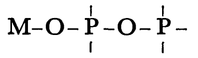
to be a part of the structure of the hydrates and anhydrides, respectively. If the electron donating power of the metal atoms is adequate, the oxygen atoms in M–O linkages may be basified. Comparison of Fig. 1 with Fig. 2 indicates that the catalytic activities (basicities) of metal phosphates reach their maxima when dehydrated completely. These results are reasonably explained as follows. Since the negative charge on the oxygen of II is higher than that of I, the basicities of the anhydrides are larger than those of the hydrates, and hence the activities of the former are higher than those of the latter. In view of the valency and radius, the order of the electron donating power of alkali metal atoms is K>Na>Li and corresponds to the order of the basic strengths of tertiary phosphates: $K_3PO_4 > Na_3PO_4 > Li_3PO_4$. A portion of the structure of an acidic phosphate is probably as given below. Since the negative charge on the oxygen of II is higher compared to that of III, the basicity of a tertiary phosphate is expected



$\mathrm{M{-}O{-}\overset{|}{\underset{|}{P}}{-}O{-}H}$

III

to be superior to that of an acidic phosphate. Indeed, this prediction is confirmed by the results from basic property measurements and activity measurements. Ivanov *et al.*[2] have also reported that the activity of the neutral phosphates is greater than that of the disubstituted phosphates. No basicity or the very low activity[1] of a pyrophosphate can be attributed to the poorer negative charge on the oxygen atom in M–O linkages of IV, because the electron-withdrawing power



$\mathrm{M{-}O{-}\overset{|}{\underset{|}{P}}{-}O{-}\overset{|}{\underset{|}{P}}{-}}$

IV

of pyrophosphate ion is considered to be stronger than that of orthophosphate ion.

According to Tillmanns and Baur,[11] NaOH is built into the crystal structure of $Na_3PO_4 \cdot 12H_2O$ and its amount (0—0.25 mol) depends on the conditions under which the crystal was formed. If this is the case, it seems to deserve examination how NaOH contributes to the basicity of tertiary sodium phosphate. It was found that both NaOH and KOH initially show little basicity, but the basic colors of bromothymol blue and phenolphthalein adsorbed on the solids gradually deepen as the suspensions take up moisture. Moreover, neither dry nor wet salts converted 2,4-dinitroaniline and 4-chloro-2-nitroaniline to their conjugate bases. These results indicate that a caustic alkali is not a so-called solid base, and its concentrated solution has not so high basic strength as the surface of K_3PO_4 has. Therefore, the basic properties of metal phosphates are considered to be predominantly attributable to negatively charged oxygens on structures I—III.

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