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Glasses of Alkaline Earth Metaphosphates as Acid Catalysts: A Comparative Study with Crystalline Catalysts

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Surface properties of Mg-, Ca-, and Ba-metaphosphate glasses have been compared with those of their crystalline catalysts by investigating changes in their surface acidity and catalytic activity for 2-propanol dehydration resulting from their crystallization. All of the glassy samples contain two kinds of acid sites with different acid strengths, both of which are due to surface POH groups. The number of strong acid sites which are responsible for dehydration activity decreases significantly upon crystallization, while the number of weak acid sites remains almost constant. This reduction of surface acidity results from a solid-state condensation reaction of POH groups which always accompanies their crystallization. Thus, for the metaphosphates, glass formation is effective for increasing surface acidity. This increase is probably due to the characteristic structure of glasses. © 1993 Academic Press, Inc.

INTRODUCTION

Glassy materials are attractive to heterogeneous catalytic studies because their structures are characterized by a lack of long-range order. In recent years, the catalytic properties of amorphous metal alloys or so-called metallic glasses have been extensively studied and sometimes found to be superior to their crystalline counterparts (*1*). By contrast, the interest shown in typical glasses prepared from inorganic oxides has been limited, for example, to applications such as a catalyst support (as is seen in porous glasses) and to adsorption studies with various gases in relation to their chemical stabilities (*2*). The oxide glasses can be produced much more easily and are more stable to heat treatment than the metallic glasses, although the heat treatment must be restricted below their own glass-transition temperatures. Furthermore, there are many working catalysts of binary and more complex systems of oxides, whose compositions are in glass-forming regions (*3*). These facts suggest that oxide catalysts in the glassy state are important not only as models of working catalysts for investigating the nature of active sites, but also may have practical use.

In previous papers, we have reported the differences in catalytic activities between the glassy and crystalline states using a vanadate (V_2O_5–BaO–ZnO) (*4*), GeO_2 (*5*), and $Ca(PO_3)_2$ corresponding to a CaO–P_2O_5(1 : 1) composite (*6*). Significant increases in the catalytic activities for 2-propanol dehydration and 1-butene isomerization were observed in $Ca(PO_3)_2$ as a result of the acidity enhancement by glass formation. From the fact that the glass contains hydroxyl groups, the protons of which contribute to electrical conductivity (*7*), it was inferred that the acidity enhancement might be caused by a shortening of polyphosphate chains terminated with POH groups. Metal metaphosphates have received little attention due to their weak acidity, in contrast with other kinds of phosphates such as ortho- and pyrophosphates and some apatites. In addition, glass formation has been recognized to be a process which causes

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materials to be chemically less active. Thus, the observed enhancement in surface acidity demonstrates that glass formation is one of the possible methods for activating catalysts in some cases.

In the present work we used $Mg(PO_3)_2$ and $Ba(PO_3)_2$ in addition to $Ca(PO_3)_2$, in order to investigate if the acidity enhancement due to glass formation is generally observed for alkaline earth metaphosphates. For this purpose, changes in the surface acidity and catalytic activity for 2-propanol dehydration due to crystallization were followed by treating a glassy sample at various temperatures. In the glassy state, vertex-shared phosphate tetrahedra form long-chain structures. In the crystalline state this structure is preserved except for $Mg(PO_3)_2$, which forms a cyclic tetrametaphosphate (*8*, *9*).

EXPERIMENTAL

The three metaphosphate glasses denoted below by MgP, CaP, and BaP were prepared under atmospheric conditions by melting chemical reagent grade $Mg(H_2PO_4)_2 \cdot 3H_2O$ at 1350°C, $Ca(H_2PO_4)_2 \cdot H_2O$ at 1300°C, and $Ba(PO_3)_2$ at 1150°C, respectively. These melts were air-quenched and then ground (200 mesh under) to be used as catalysts. DTA analyses (10 K/min) with Rigaku Denki Thermoflex showed that glass transition temperatures (T_g) were 563°C for MgP, 540°C for CaP, and 487°C for BaP. The temperatures of crystallization on prolonged heating (15 hr) were checked with Rigaku Denki Geigerflex (CuK_α radiation) and found to be slightly higher than their own T_g's. The resulting crystals were $Mg_2(PO_3)_4$ and polyphosphates in the forms of β-$Ca(PO_3)_2$ and $Ba(PO_3)_2$. A trace amount of the γ-phase was also observed in the CaP sample crystallized at 600°C, but it disappeared at higher temperatures.

The catalytic activity was characterized by studying the decomposition of 2-propanol in a static system using a high-vacuum apparatus, and pressure increases due to the reaction were followed by manometric measurements. Products were analyzed by GC (Yanaco Co. G-2800) using a BX-10 column. Prior to each run, about 1 g of glassy sample (0.3–0.5 m^2/g) was heat treated in dry atmospheric air for 15 hr at the temperature which was varied stepwise from 300 to 700°C, evacuated for 1 hr, and then cooled to the reaction temperature (230°C and three other temperatures selected in the range 180–250°C for determining the activation energy). Since all of the glassy samples were heavily sintered by treating above T_g, as is generally observed in glassy materials (*4*, *5*), they were ground again for further use. Surface areas were determined by volumetric adsorption of Kr at −196°C.

Surface acidity was measured by temperature-programmed desorption (TPD) of *n*-butylamine in flowing He (100 ml/min). This technique was also applied to CO_2 and 2-propanol for evaluating surface basicity and the active sites for alcohol decomposition, respectively. The catalyst pretreated at desired temperatures was first saturated with each of the gas and vapors (20 Torr) in a static aparatus at 200°C (butylamine, CO_2) or room temperature (2-propanol, CO_2). After evacuation at the same temperature for 1 hr, the catalyst was exposed to the He flow. A U-shaped trap connected between a sample cell and the detector was used, when needed, to remove condensable materials from the effluent by cooling it with dry ice and methanol. The TPD data were collected with an electonic integrator (SIC, chromatocorder) connected to a TCD detector. The TPD peak area was calibrated with a known amount of the effluent, for which its GC peak was obtained by passing through a Porapak QS column and the detector operating at the same conditions as in the TPD run. 2-Propanol and *n*-butylamine (guaranteed grade, Wako Pure Chem. Co.) were purified further by dehydration with $CaCl_2$ and CaH_2, respectively, and by subsequent bulb-to-bulb distillation in a high-vacuum apparatus. CO_2 (99.999%, Takachiho Chem. Co.) was used without further purification.

The solid-state condensation reaction of POH groups present in the glassy catalysts was investigated by monitoring the formation of water on heating them in a programmed manner, using the apparatus for the TPD experiments. Weight losses due to the reaction were measured with a Cahn electrobalance.

RESULTS AND DISCUSSION

Catalytic Activity

All of the glasses (MgP, CaP, and BaP) catalyzed exclusively the dehydration of 2-propanol, and the extremely high selectivity was preserved after they had crystallized. In every run the total pressure increased linearly in the initial stage (at least below 30% conversion) as the reaction proceeded. The initial rate obtained from the slope of a reaction curve did not vary in repeated runs. This indicates active sites present on these catalysts to be very stable and at the same time excludes the production of new active sites during the reaction under the present conditions. In fact, preliminary treatment of the catalysts with H_2O (16 Torr) at the reaction temperature for 1 hr revealed no effect on the catalytic activity of CaP. Crystalline $Ba(PO_3)_2$ powder was also used directly from a commercial source for comparison, and is denoted by BaP[C]. On this sample, the initial rate of the reaction decreased rapidly with repeated usage, attaining a stationary value after several runs.

Figure 1 shows changes in the specific activity represented by the initial rate per unit area at 230°C as a function of the temperature of pretreatment, where steady-state activities are plotted for the BaP[C]. It is interesting to note that the three glasses reveal the same behavior toward heat treatment. That is, the activity increases gradually with an increase in the temperature, and decreases abruptly at a critical temperature (about 600°C for MgP, 550°C for CaP, and 500°C for BaP). These temperatures agree well with those of their respective crystallization on prolonged heating, so that the significant decrease in activity is suggested to be due to crystallization. This is confirmed by the result obtained for the BaP[C], which does not show a large activity drop. A simple comparison of the activities shows that the glassy samples are about 20 times more active than the crystallized ones, as can be seen later in Table 2. One might expect that the higher activity in the glassy state would arise from a mechanochemical effect which is induced in a process of pulverizing catalysts and not removed by pretreatment below T_g. This effect, however, proved to be unimportant from separate experiments with an unground sample of CaP, since its activity decreased to nearly the same extent as in the powdered samples. Consequently, the observed difference between the glassy and crystalline states is considered to arise essentially from the difference in their structures.

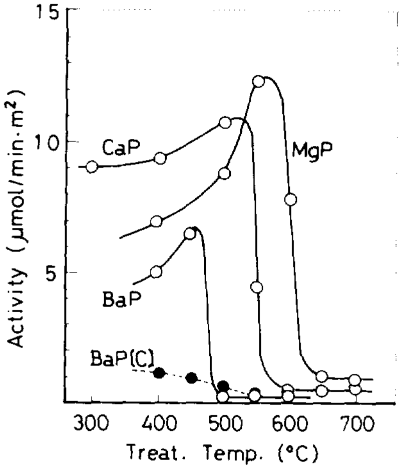

FIG. 1. Changes in catalytic activity for 2-propanol dehydration at 230°C by heat treatment of BaP, CaP, and MgP glasses and crystalline BaP[C].

An activation energy for the dehydration reaction was determined from an Arrhenius plot of ln V_0 (initial rate) against $1/T$. The value of $E_a = 25$ kcal/mol was obtained in MgP, which increased to 28 kcal/mole after crystallization. Similar tendencies were observed in the other glasses; an increase from $25 \sim 27$ to $30 \sim 32$ kcal/mole in CaP and from $30 \sim 32$ to $33 \sim 35$ kcal/mole in BaP. This energetic factor must be considered to explain the activity changes due to crystalli-

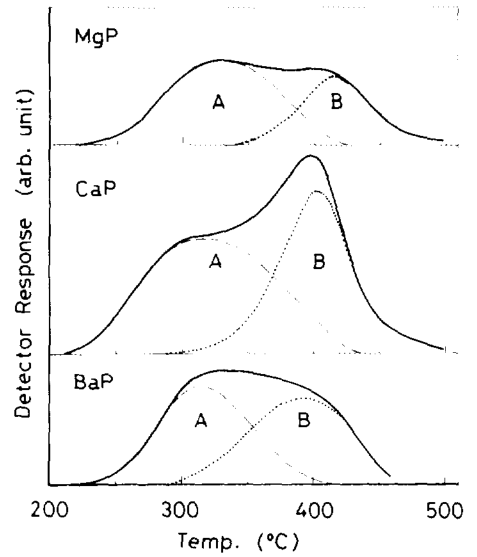

FIG. 2. TPD curves of *n*-butylamine on glassy samples pretreated at 500°C (MgP, CaP) or 450°C (BaP): ——, original curve; ···· (B peak), detection through a dry-ice/methanol trap. Dashed line (A peak) was obtained by subtracting B from original curve. Heating rate was 10°C/min.

zation. Another point to note is that the above values are very close to the energy of 30 kcal/mole which has been observed for the same reaction on calcium ortho- and pyrophosphates (*10*).

Surface Acidity and Basicity

Figure 2 shows three sets of typical TPD curves (solid lines) of *n*-butylamine on the glassy samples pretreated at 500°C (MgP and CaP) or 450°C (BaP). The curves are all very broad, but two peaks denoted A and B are clearly seen in the curve for CaP. In fact, the B peak was separately observed for all of the samples by passing the effluent through the cold trap before detection, as shown by the dotted lines. Thus, the A peak can be drawn by subtracting the B peak from the original curve obtained without the cold trap, which enabled us to measure separately the peak areas. GC analyses showed that the B peak arises from the decomposition products NH_3 and butenes, while the A peak arises from molecular desorption of *n*-butylamine. The ratio of the A peak area to the B peak area was not affected by changing the heating rate from 2 to 15°C/min. Moreover, NH_3 showed almost the same TPD profiles as the amine. These findings suggest the presence of two distinct acid sites, which will be refered to as A (weak) and B (strong) sites. The presence of two kinds of acid sites with different acid strengths has been already observed on amorphous and crystalline samples of zirconium phosphate by Hattori *et al.* (*11*) and Clearfield and Thakur (*12*). The former authors showed further by IR spectroscopy that both types of acid sites are due to surface POH groups. This might be the case in the metaphosphates.

Figure 3 shows relative changes in the peak areas (A and B) and the catalytic activity as a function of the temperature of pretreatment for a sample of BaP. The area of the B peak decreases significantly by pretreatment above the temperature of crystallization, while that of the A peak remains almost constant. These changes are quite similar to those observed in CaP (*6*) and in MgP. The striking parallelism between the changes in the catalytic activity and in the area of the B peak indicates that the number

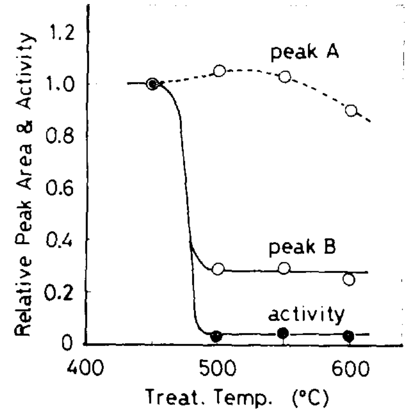

FIG. 3. Relative changes in catalytic activity and in integrated areas of TPD peaks of *n*-butylamine resulting from heat treatment of BaP (see text).

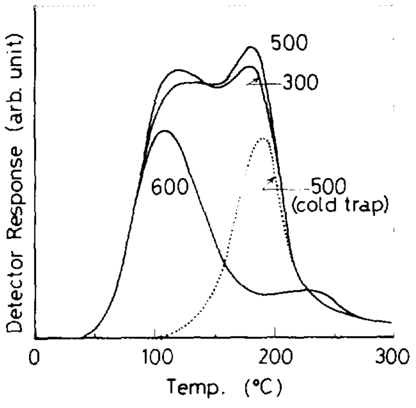

FIG. 4. TPD curves of 2-propanol on CaP after pretreatment at 300, 500, and 600°C (dotted line; typical detection through a dry-ice/methanol trap). Heating rate was 10°C/min.

of the B sites is another important factor affecting the catalytic activity. The contribution of B sites to the catalytic activity will be discussed later in more detail.

The TPD experiments with CO_2 showed no irreversible adsorption at room temperature and 200°C on all of the catalysts used here. This suggests the absence of effective basic sites, which is consistent with the fact that they exhibit no catalytic activity in the dehydrogenation of 2-propanol. Tada (*13*) and Nozaki and Kimura (*14*) have not observed any basic sites with $H_0 \geqq +7.1$ on $Ca(H_2PO_4)_2$ calcined at 400 and 500°C, respectively, at which the material must be converted into $Ca(PO_3)_2$ (*15*). These observations provide an indirect proof for the absence of basic sites on metaphosphates.

Active Sites for 2-Propanol Dehydration

In order to clarify the contribution of the two acid sites (A and B) to the catalysis, TPD experiments with 2-propanol were performed on fresh and amine-covered surfaces of CaP.

Figure 4 shows TPD curves of 2-propanol (solid lines) from a fresh surface pretreated at various temperatures. Two distinct peaks are seen. Remarkable changes due to crystallization are observed in a high-temperature peak (compare the curves for 500 and 600°C treatment): a significant decrease in the intensity and a shift in the peak maximum to higher temperature. A decomposition product, propene, was present exclusively in the high-temperature peak, which enabled us to isolate this peak from the other using the cold trap, as shown typically for 500°C treatment by the dotted line. The maximum temperature (T_M) of the peak thus isolated was used to evaluate an activation energy for a temperature programmed reaction (TPR) of chemisorbed 2-propanol. From the plots of $\ln(T_M^2/\beta)$ against $1/T_M$ at several different heating rates (β), the values of E_a = 22 and 32 kcal/mole were obtained in the glassy and crystalline states, respectively. These values are quite similar to those obtained for the catalytic reaction, which confirms that the surface sites associated with the high-temperature peak are solely involved in the catalytic reaction.

TPD of 2-propanol on a surface covered with *n*-butylamine was carried out after the following adsorption procedure: The amine was adsorbed at 200°C, followed by evacuation at various temperatures in the range of 200–500°C to vary its surface coverage, and by subsequent adsorption of 2-propanol at room temperature. In every run, the cold trap was used to remove molecular-desorption peaks from TPD curves. The resulting curves are shown in Fig. 5. The high-temperature peak from 2-propanol decomposition grows with increasing the temperature of evacuation, or with decreasing surface coverage of amine. Integration of the calibrated peak areas for 2-propanol and *n*-butylamine decomposition products yielded results plotted in Fig. 6. The inverse correlation of slope = −1 shows that the same surface sites are involved in each reaction. Thus, the B site is responsible for dehydration activity. These sites may also catalyze dehydration for crystallized samples, because of the close agreement between the activation energies determined for the catalytic reaction and for the TPR of chemisorbed 2-propanol.

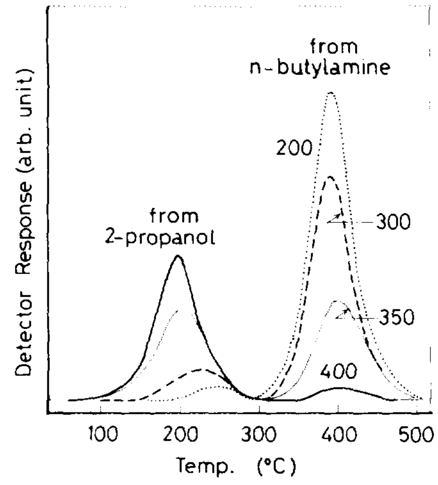

FIG. 5. TPD curves for sequential adsorption of *n*-butylamine and 2-propanol on CaP pretreated at 500°C. Surface coverage of *n*-butylamine was changed by evacuating at temperatures indicated before 2-propabol adsorption at room temperature. Heating rate was 10°C/min.

TABLE 1

The Number of Acid Sites ($\times 10^{-17}/m^2$)

Sample form	CaP(1)		CaP(2)		CaP(3)		BaP	
	A	B	A	B	A	B	A	B
Glass[a]	2.7	3.0	2.2	2.7	4.0	3.5	2.0	2.1
Cryst.[b]	2.0	0.7	2.0	0.5	2.2	0.7	1.8	0.5

[a] Pretreated at 500°C (CaP) or 450°C (BaP).
[b] Pretreated at 600°C.

Table 1 summarizes the number of the acid sites on CaP and BaP samples, which was determined on the basis of the additional assumption that one site is involved in the chemisorption and desorption of one *n*-butylamine molecule. The reproducibility of activity numbers is indicated in Table 1. From these data, turnover numbers (molecules/sec · B-site) at 230°C were evaluated for the samples of CaP(1) and BaP. The results are listed in Table 2, together with their specific activities extracted from Fig. 1. It is interesting to note that the activity of the B site is reduced to about ⅕ after crystallization in both CaP and BaP as a result of an increase in the activation energy for the reaction.

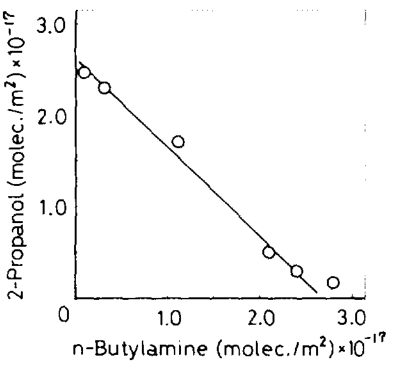

FIG. 6. Correlation between the amount of chemisorbed 2-propanol giving the high-temperature TPD peak and the amount of *n*-butylamine giving the B peak on CaP pretreated at 500°C.

Solid-State Condensation Reaction in Relation to Surface Acidity

According to a thermogravimetric analysis using the electrobalance, the glasses underwent a continuous weight loss with increasing activation temperature, that was accelerated above T_g. Figure 7 shows H_2O-formation curves observed with a TCD detector, on heating glassy samples from the temperature of pretreatment (450°C for BaP, 500°C for MgP and CaP) to 700°C. These curves correspond to weight losses of about 0.04, 0.07, and 0.08% for MgP, CaP, and

TABLE 2

Activities and Turnover Numbers at 230°C

Sample		Activity (mole/sec · m²)	Turnover number (molec./sec · B-site)
Cap(1)	Glass	1.8×10^{-7}	0.36
	Cryst.	0.9×10^{-8}	0.08
BaP	Glass.	1.1×10^{-7}	0.32
	Cryst.	0.5×10^{-8}	0.06

Note. For treating conditions, refer to Table 1.

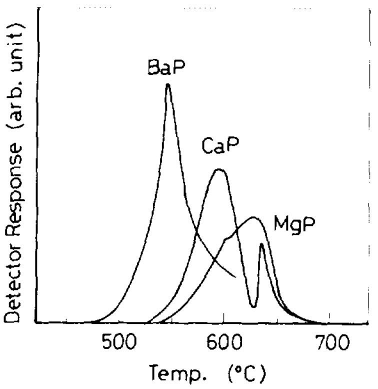

FIG. 7. H_2O-formation curves from glassy samples pretreated at 500°C (MgP, CaP) or 450°C (BaP). Heating rate was 5°C/min.

BaP, respectively. The formation of water clearly indicates the occurrence of the condensation of POH groups. Therefore, extended phosphate chains are formed during crystallization, except for MgP which transforms into a crystal with a cyclic structure. This chain extention on crystallization is supported by observations of Ohashi and Van Wazer (*16*) who reported 20 P atoms per chain for glassy CaP, 200 ~ 400 P per chain for γ-CaP and 10,000 P per chain for β-CaP. The second peak is seen only in CaP. This peak was reduced with the duration of pretreatment at 500°C. Moreover, a small amount of the γ-phase was observed by XRD when heating had been interrupted at 620°C, but not at 700°C. These findings indicate that the second peak is ascribed to the phase change from the metastable γ-phase, which is formed probably as an intermediate, to the β-phase. The formation of water during this process can be explained by the difference in the chain length between the phases, though not analyzed quantitatively.

The samples crystallized after the above experiments were converted again into the glassy state by melting them under atmospheric conditions. In Fig. 8, the formation of water from CaP thus obtained is shown by curve (c), comparing with the results for the original glass (a) and the crystallized sample (b). The H_2O peaks are completely eliminated by crystallization, but are restored with slightly shifted peak maxima by glass formation. The same results were obtained for MgP and BaP. Therefore, a chain shortening is suggested to take place in the melting process, which can be rationalized by the well-known fact that molecular vibration is too severe to maintain long chains at high temperatures. Thus, the chain length and –OH content might be varied by controlling the temperature, duration, water vapor content of the atmosphere, etc., during melting (*3*).

The condensation reaction involves mainly POH groups with strong acidity which correspond to the B site (Fig. 3). As for the concentration of surface POH groups, Clearfield and Djuric (*17*) have already reported that each of them occupies 23.99 Å^2 on the layered plane of α-zirconium acid phosphate, which corresponds to 4.17 × 10^{18} OH/m^2. Moreover, 2.9 × 10^{18} OH/m^2 have been reported by Turco *et al.* for zirconium pyrophosphate (*18*). The number of the acid sites (A + B) per unit area of the metaphosphates (Table 1) are an order of magnitude smaller than those expected from their results. This discrepancy may result from the difference in the experimental methods. In

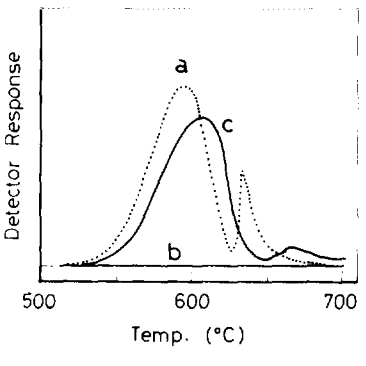

FIG. 8. Comparison of H_2O-formation curves from CaP pretreated at 500°C: (a) original glass, (b) crystallized sample obtained by heating (a) to 750°C, and (c) glass prepared by remelting (b). Heating rate was 5°C/min.

the present study, *n*-butylamine was evacuated at 200°C before the TPD run so that weak acid sites are not counted. *N*-butylamine titration with methylred as a Hammet indicator was used to determine that the total amounts of acid sites with $H_0 \leqq +4.8$ were 4.0 and $3.2 \pm 0.2 \times 10^{18}$ sites/m^2 for glassy and crystallized samples of CaP, respectively. These values are nearly the same as those for surface POH groups reported by the above authors, suggesting that the A and the other weaker sites might be also attributed to POH groups.

It is clear from the above considerations that some of the protons of POH groups in the metaphosphates increase their Brönsted acidity by glass formation. The most characteristic features of glassy materials are a lack of long-range order and a distribution in P–O bond strength. Such structural heterogeneity may influence POH acidity. Moreover, stress remaining in a quenched glass may affect acidity. While chain length affects the number of acid sites, it may also influence intrinsic acidity. We believe that the intrinsic acidity of the B site can be roughly estimated from activation energies for 2-propanol dehydration. The energies obtained for the metaphosphates, 25 ~ 35 kcal/mol, are significantly higher than those for zirconium acid phosphates, 10 ~ 13 kcal/mol (*12, 19, 20*). This difference suggests that the B site is a weaker Brønsted acid than the active sites on the zirconium phosphates, which are surface POH with the acid strength of $-3.0 \geqq H_0 \geqq -5.6$ (*11, 12*). Experiments for measuring the acid-strength distribution of POH groups are now in progress to gain a better understanding of the activity difference between the glassy and crystalline states of the metaphosphates.

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