Enhancement of surface acidity and catalytic activity by glass formation of calcium metaphosphate

N. Yoshida, Y. Kimura, M. Sugimoto and S. Kishimoto

Department of Chemistry, Faculty of Science, Kobe University, Nada-Ku, Kobe 657, Japan

Received 17 July 1991; accepted 8 August 1991

Effective acid sites for the dehydration of 2-propanol and isomerization of 1-butene were found to be generated by glass formation of calcium metaphosphate. The number of these sites with strong acidity remarkably decreased by the crystallization of the glass, where the condensation of hydroxyl groups were significant. Thus, the sites must be the monohydrogen phosphate protons.

Keywords: Calcium metaphosphate glass; surface acidity; catalytic activity

An understanding of the surface properties of glassy materials is of great importance in relation to their catalytic properties. Much attention has been paid to metallic glasses for the last ten years [1], but little to typical inorganic glass-forming materials. Previously, we have observed the different catalytic properties of vanadate, V_2O_5-BaO-ZnO [2], and GeO_2 [3] glasses from their crystalline counterparts. However, the nature of the surface sites could not be clarified. Now, we have extended our studies to calcium metaphosphate, $Ca(PO_3)_2$. We found that this glass possesses higher content of strong acid sites on its surface than the corresponding crystal, and exhibits superior catalytic properties.

Glassy samples of calcium metaphosphate were prepared by melting dibasic calcium phosphate for 3 hr at 1250 ° C, air- quenching, and then grinding. The glass transition temperature, T_g was 545 ° C, according to thermal analysis. It was also confirmed that crystallization to β-$Ca(PO_3)_2$ occurs after prolonged heating above 550 ° C. Information on surface acidity was obtained from temperature programmed desorption (TPD) of n-butylamine in He (100 ml/min), using a TCD detector. The amine was preliminarily adsorbed for 1 hr at 200 ° C under pressure kept at 20 Torr. The decomposition of 2-propanol (230 ° C) and isomerization of 1-butene (195 ° C) were carried out as test reactions in a static system at an initial pressure of 25 Torr. The initial reaction rate per unit area

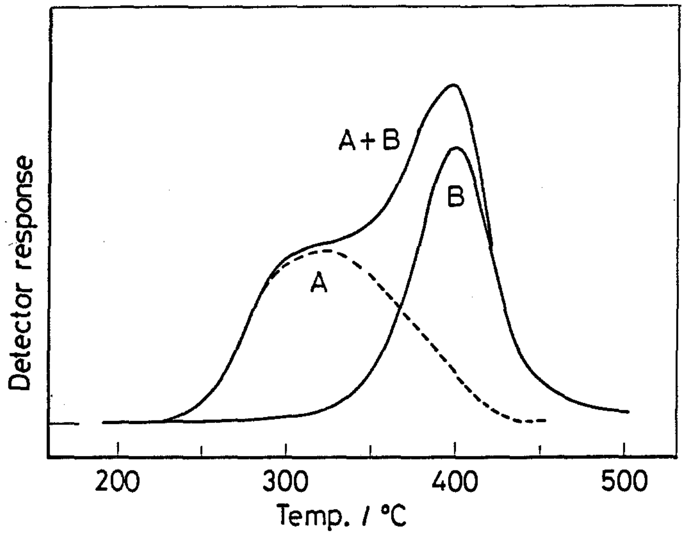

Fig. 1. TPD curve of n-butylamine on $Ca(PO_3)_2$ glass (A+B); molecular desorption (A), decomposition products (B). Treatment 500 ° C, heating rate 10 ° C/min.

was adopted as a measure of catalytic activity. Prior to each run, a powdered sample was treated for 1 hr with atmospheric dry air at various temperatures between 300 ° C and 700 ° C, and then evacuated for 1 hr. The BET-surface area was determined by volumetric adsorption of Kr at −196 ° C.

Curve A + B in fig. 1 shows a typical TPD curve of n-butyl-amine on a glassy sample. There are two distinct peaks, indicating that it contains two types of acid sites on the surface. In a separate experiment, no adsorption of NO was observed. Since this material is known to be adsorbed only on Lewis acid sites [4], both of the observed sites are considered to be Brønsted acid sites with different acid-strengths. This finding corresponds to that of Hattori et al. [5], who have observed two Brønsted acid sites of $+4.8 \geqslant H_0 \geqslant +3.3$ and $-3.0 \geqslant H_0 \geqslant -5.6$ on zirconium phosphates. These sites are referred to as A site (weak) and B site (strong), below. GC-analysis showed that the A peak arises from the desorption of molecular n-butylamine and the B peak from the decomposition products, NH_3 and butenes. The B peak is successfully separated by cooling a U-shaped trap in a flow path between the TPD cell and detector at −78.5 ° C (curve B). Thus, the A peak (shown by the broken line) can be obtained by subtracting the B peak from the original curve (A + B).

Curves A and B in fig. 2 show relative changes in the integrated areas of the two peaks with the temperature of pretreatment, where they are given for the same area. The area of the B peak decreases significantly by treating above 550 ° C, where the glass transforms into the β-crystal, while that of the A peak is held almost constant. Thus, it is clear that the B site is significantly diminished by its crystallization. In order to show this change quantitatively, the amount of

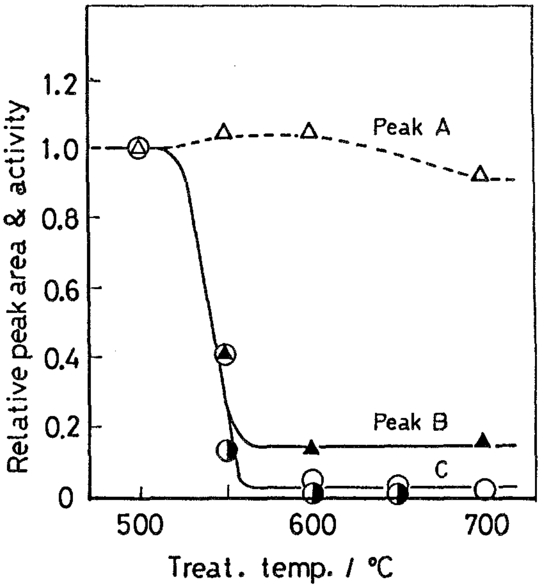

Fig. 2. Relative changes in areas of TPD peaks (A, B) and catalytic activities (C) by heat-treatment; ○ Decomposition of 2-propanol, ◑ isomerization of 1-butene.

the acid sites was estimated by calibrating the area of each peak in the number of molecules desorbed and by assuming that one molecule of of n-butylamine could be adsorbed on one site. The obtained values are as follows:

500 °C-treat.(glass)	A: 2.2; B: 2.7×10^{17} sites/m^2
600 °C-treat.(crystal)	A: 2.3; B: 0.5×10^{17} sites/m^2.

Calcium metaphosphates were extremely selective toward the dehydration of 2-propanol in both glassy and crystalline states. In the isomerization reaction, the ratio of cis- and trans-2-butene remained constant throughout the reaction ($c/t = 0.67$ for the glass and 0.5 for the crystal). As shown by curve C in fig. 2, the catalytic activities in these reactions change in the same manner as the area of the B peak by the pretreatment. This suggests that the B site is responsible for the activities.

The participation of the acid sites in the dehydration of 2-propanol was investigated also by poisoning experiments with n-butylamine on a glassy sample. The results are shown in fig. 3, where the relative activity is plotted against the temperature of evacuation (1 hr) of the sample preliminarily saturated with the amine. As can be seen from comparison with the TPD peaks of n-butylamine obtained at 2 °C/min, the activity can be restored by the desorption of the amine only from the B site. This supports the negligible participation of the A site in the reaction. Consequently, another finding in fig. 2 that crystallized samples exhibit lower activities than the expected value from the number of the

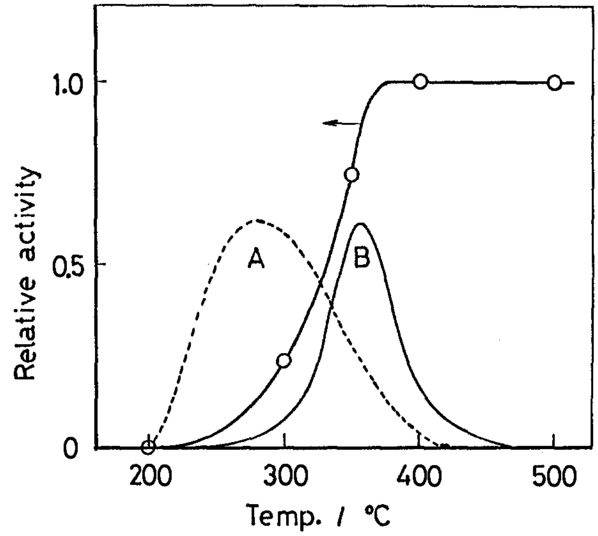

Fig. 3. Relative change in activity by poisoning with n-butylamine (abscissa: temperature of evacuation after poisoning), and separated TPD peaks at 2 ° C/min (A), (B).

B site suggests that its acid-strength would be reduced by the crystallization.

Surface acidity may be affected by the change in the surface compositions. However, XPS analyses showed no difference between glassy and crystalline samples, not only in the atomic ratio of P/Ca but also in their binding energies.

Another factor which may be considered is a poly-condensation reaction. According to Ohashi and van Wazer [6], glassy and β-crystalline calcium metaphosphates consist of various sized chain anions, having a weight averaged number of phosphorus atoms equal to ca. 20 and 10,000, respectively. In the present experiments, a weight-loss of about 0.1 wt% was observed on the crystallization of the glassy sample. Therefore, the significant decrease in the amount of the B site can be explained by the condensation of P-OH groups on the chain ends to form longer chains upon crystallization. Similar phenomena have been observed in amorphous and partially crystallized zirconium phosphates, where pyrophosphate is formed by the condensation [7]. These considerations lead us to the conclusion that glass formation generates additional protonic sites (P-OH) with strong acidity through breaking and shortening of phosphate chains on the surface of metaphosphates, which has so far been known to be inactive for acid-catalyzed reactions. This effect is also expected for other phosphate glasses.

References

[1] A. Molnar, G.V. Smith and M. Bartok, Adv. Catal. 36 (1989) 329.
[2] N. Yoshida, K. Kazehara, Y. Kawamoto and S. Kishimoto, Chem. Lett. (1979) 667.

[3] N. Yoshida, K. Miyataka and S. Kishimoto, J. Catal. 88 (1984) 237.
[4] K. Tanabe, *Solid Acid and Base* (Kodansha, Tokyo; Academic Press, New York, 1970).
[5] T. Hattori, I. Ishiguro and Y. Murakami, J. Inorg. Nucl. Chem. (1978) 1107.
[6] S. Ohashi and J.R. van Wazer, J. Am. Chem. Soc. 81 (1959) 830.
[7] A. Clearfield and D.S. Thakur, J. Catal. 65 (1980) 185.