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The Preparation and Some Properties of High-Surface-Area Boron Phosphate

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The preparation and some properties of high-surface-area boron phosphate have been studied. The effect of reaction parameters on the surface area of boron phosphate produced by the reaction of tri-*n*-propyl borate and orthophosphoric acid has been examined, and some surface and bulk properties of the solid have been studied. A one-to-one P_2O_5/B_2O_3 ratio produced a surface area of approximately 200 m^2 g^{-1}. Aging of the samples at room temperature for 500 days in screw cap vials and sealed glass tubes reduced the surface area by approximately 35 and 20%, respectively. Evacuation at temperatures up to 500°C produced a weight loss of approximately 10%, while the surface area increased to 220 m^2 g^{-1} at 300°C.

INTRODUCTION

Boron phosphate has, among other things, some interesting catalytic properties, particularly in reactions involving the loss of water (*1*). The most convenient method of preparation of this solid involves the use of boric and orthophosphoric acid. However, experience in this laboratory suggests that surface areas greater than approximately 50 m^2 g^{-1} are not attainable in this way, and for other studies high-surface-area boron phosphate was required. The reaction of tri-alkylborate and orthophosphoric acid has been reported to produce a solid of suitable surface area (*2*, *3*). Since relatively little details of this preparation and the properties of the resulting solid have been given previously, some investigations were conducted to discover the preparation parameters which would produce boron phosphate of maximum surface area. In addition, experiments were performed to examine the long term change in surface area of these high-area boron phosphate samples at room temperature as well as the change at higher temperatures and shorter periods of time. Nitrogen adsorption isotherms were measured, and changes in weight and surface area on evacuation were also obtained.

METHOD

High-surface-area BPO_4 was prepared by mixing and heating appropriate amounts of tri-*n*-propyl borate and 85.6% orthophosphoric acid (both as received) in a stirred reactor contained in a heated oil bath. When the temperature of the bath reached 120°C, the cap on the reactor was removed to allow the *n*-propanol and water vapor to escape. The temperature was maintained at 120–130°C for ¾ hr, or until the product was almost dry. It was then removed and dried at 110°C for 3 hr in a vacuum oven under aspiration. The product was ground, sieved through a 100-mesh screen, and the fines were stored in a screw cap vial. A variety of molar ratios of P_2O_5/B_2O_3, as calculated from the initial amounts of reactant used, were employed in the preparations.

All isotherms were measured by using a standard calibrated quartz spring apparatus and surface areas were calculated from nitrogen isotherms, obtained at liquid nitrogen temperatures, by applying the BET theory. The adsorption apparatus could be fitted with a tubular furnace for heating the samples, if necessary.

For examination of aging over long periods of time, ½ g samples of boron phosphate were each evacuated for 15 min at room temperature and then heat sealed in their glass containers while still under vacuum. The surface area of these samples was measured periodically by rupturing the vials as needed. For comparison purposes, a measurement of surface area was also performed on a large sample stored in a screw cap vial and opened for each measurement.

For measurements of weight loss and change in surface area on heating, a sample was placed in the quartz spring balance, its surface area determined, heated at a fixed temperature in vacuum for 12–14 hr, and its surface area redetermined. The process was repeated by heating to progressively higher temperatures with the same sample.

RESULTS AND DISCUSSION

The results of the experiments performed to determine the effect of preparation conditions on the surface area of boron phosphate are summarized in Table 1. These results show that the maximum surface area is obtained if the P_2O_5/B_2O_3 ratio is approximately 1:1.06 with the products being mixed at room temperature and heated to 120–130°C for about ½–1 hr, with no refluxing.

The change in surface area of boron

TABLE 1

EFFECT OF PREPARATION CONDITIONS ON THE SURFACE AREA OF BORON PHOSPHATE

Sample No.	P_2O_5/B_2O_3 molar ratio	Preparation temp (°C)	BET surface area (m^2/g)	Method of preparation[a]
BP(TB-2)	1.22	120	54	TB[b] heated 120°C in reactor, HP[c] 120°C in beaker, mixed, heated and stirred 1 hr, dried 110°C for 2 hr
BP(TB-3)	1.06	120	198	TB mixed with HP, heated to 120°C 40 min. Kept 10–20 min, dried 80–90°C for 2 hr
BP(TB-4)	1.21	120	105	Same as BP(TB-3) except dried overnight at 70°C
BP(TB-5)	1.02	120	180	Same as BP(TB-3) except dried at 80°C for 3 hr
BP(TB-6)	1.00	140	180	Heated in 1 hr to 140°C, dried 85°C under aspiration
BP(TB-7)	1.00	140	95	Heated in 1 hr to 120°C, 1 1/2 hr at 140°C under reflux. Dried 85°C for 8 hr
BP(TB-8)	1.00	120	189	Heated to 120°C for 1 1/2 hr, dried 4 hr at 85°C. Kept 1/2 hr
BP(TB-9) BP(TB-10) } BP(TB-9,10)	1.00	120–130	(no immediate SA)	Heated to 120°C, 1/2 hr, heated 120–130°C for 3/4 hr, dried 3 hr at 110°C
BP(TB-11)	1.19	120	69	Same as BP(TB-8); dried 4 hr at 115°C
BP(TB-12)	0.80	120–130	138	30.0 g TB, 18.2 g HP, 2.46 g HB[d] mixed, heated to 120°C in 3/4 hr, kept 120–130°C for 1/2 hr, dried 4 hr at 115°C

[a] All samples dried under aspiration.

[b] TB: tri-*n*-propyl borate (K & K).

[c] HP: 85.6% phosphoric acid (Fisher Sci. Co.).

[d] HB: boric acid (Fisher Sci. Co.).

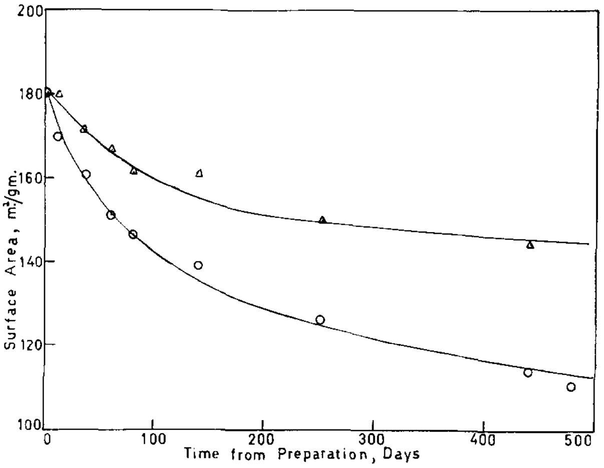

FIG. 1. Aging of boron phosphate BP(TB-3): change of surface area with time. (○) BP(TB-3) stored in screw cap vial; (△) BP(TB-3) stored in evacuated vial.

phosphate as a result of aging at room temperature is displayed in Fig. 1. It is quite evident that, in terms of preservation of surface area, storage in sealed tubes is much superior to that in screw cap vials. Over a period of 1 yr, the sample stored in the screw cap vial suffered a loss of approximately 34% in surface area, while the samples in the evacuated vials decreased 20%. It is interesting to note that, although the most rapid decrease in surface area occurs within 6 mo, there is no evidence that the area has become constant even up to 500 days with either of the storage methods. Although a mechanism for the process by which the surface area decreases is not available, nevertheless there is evidence (*4*) that the presence of water is beneficial to such a process. Presumably the process is one of sintering, a surface layer being rendered more mobile by the dissolution and/or hydrolysis of the surface of the solid in water. Nitrogen adsorption and desorption isotherms suggest that the high-surface-area BPO_4 has an open, but relatively nonporous structure.

Figures 2 and 3 show the loss in weight and the corresponding change in surface area as a function of heating temperature. Two aliquots of the same sample were

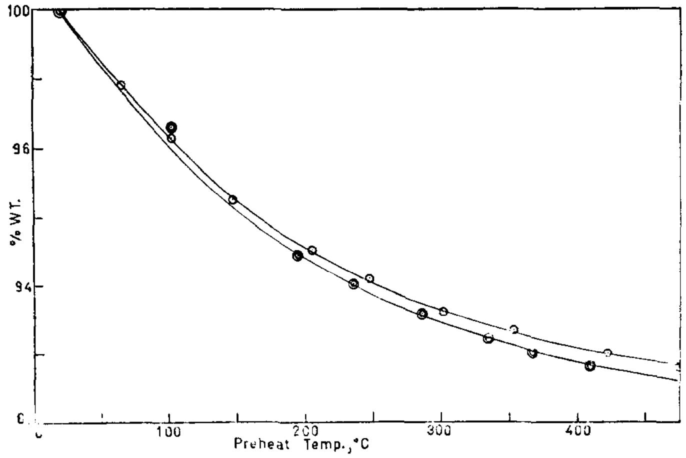

FIG. 2. BP(TB-8) weight loss on heating (relative to BP(TB-8) evacuated room temperature). (⊙) BP(TB-8) 4 days after preparation; (○) BP(TB-8) 34 days after preparation.

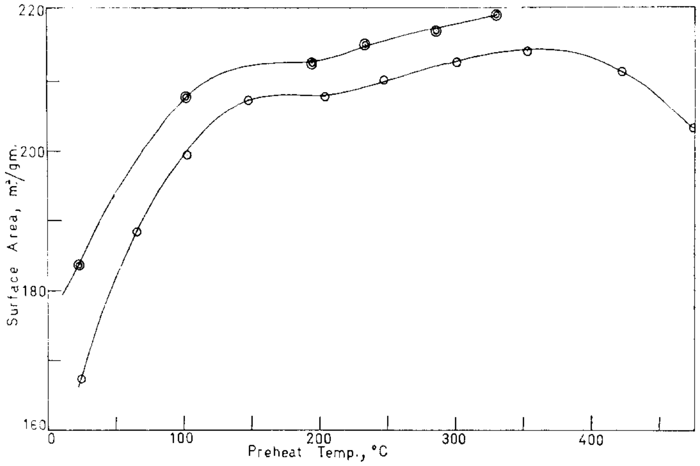

FIG. 3. BP(TB-8) change in surface area on heating. (⊙) BP(TB-8) 4 days after preparation; (○) BP(TB-8) 34 days after preparation.

studied, one selected 4 days, the other 34 days after preparation. The weight loss curves of these two aliquots are nearly coincident, both showing a loss of weight as the temperature increases to approximately 500°C. In both cases, the weight decreases more rapidly at temperatures below 200°C, but even at approximately 500°C a constant value had not been attained. Presumably most of the weight loss is due to evaporation of water produced in the preparative process, but at higher temperature some phosphoric acid (or P_2O_5) may also be eliminated.

The curves illustrating the change in surface area with temperature for the two aliquots are of the same general shape, both showing substantial increases up to about 200°C, followed by a slower, almost linear increase up to 350°C, and, finally, at least for one aliquot, a subsequent decrease in surface area. It is believed that the initial increase of surface area may be attributed to a fine structure generated as a consequence of the water attempting to leave both the surface and the bulk of the solid and in so doing producing a "popcorn" effect. The eventual decrease in surface area probably results from a partial destruction of the fine structure as well as an agglomeration of the particles themselves.

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