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Application of Scanning Electron Microscopy to the Study of the Changes in the Morphology of the Catalyst Boron Phosphate on Adsorption of Water Vapor

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Surface and bulk changes of solid boron phosphate on adsorption of water vapor have been examined with the scanning electron microscope. Amounts of water vapor up to 6% decreased the surface area up to 25% and appeared to be the result of changes in surface fine structure. More massive adsorption of water produced changes in both the surface and bulk structure of the particles of solid.

1. INTRODUCTION

The scanning electron microscope (SEM) offers some interesting possibilities in the study of surfaces of solid catalysts. To date, relatively few applications of the SEM to catalytic studies have been made. Recently, however, there are evidences of increased interest. Reimschussel and Fredericks (*1*) have examined the surface structure of alumina, complex aluminates and a mixture of both, and have observed the effects of various thermal treatments using the SEM. Anderson and co-workers (*2*) demonstrated that in the alumina trihydrate-rich Raney nickel, the trihydrate is in the form of a crystalline deposit covering most of the catalyst surface.

Surface and catalytic work from this laboratory (*3*) has been primarily concerned with boron phosphate and especially with its capabilities as a catalyst in dehydration reactions. Studies of the adsorption of water have been carried out (*4*) in an effort to gain further insight into the apparent affinity of the surface for water. Such studies demonstrated that, while some of the adsorbed water can be desorbed, most of the water is chemisorbed and cannot readily be removed, and in addition, that substantially larger quantities of water are apparently chemisorbed that would be predicted on the basis of monolayer coverage. Further, the adsorption of water resulted in measurable changes in surface area. The data available suggested that the water, on adsorbing, caused a scission of the oxygen "bridges" on the surface of BPO_4 and resulted in two surface hydroxyl groups in its place. While this mechanism might partially explain the observations, further insight into the cause of the change in surface area was needed. Here the SEM appeared to be a most valuable tool for the examination of the particles of BPO_4 and their surfaces and the effect of exposure to water vapor.

2. EXPERIMENTAL

All the electron photomicrographs were obtained with a Cambridge Instruments Stereoscan (Model 2A). The samples of boron phosphate were prepared from boric acid and orthophosphoric acid in the molar ratio of 1:1.30 by a standardized procedure used in this laboratory (*5*). The method involves the heating of the mixed reagents at 60°C for 6 hr with continuous stirring followed by an evacuation at room temperature for 24 hr. One sample was not treated further while a second sample was subjected to a thermal treatment at 400°C with evacuation prior to use. Powder X-ray diffraction patterns of this material when compared with those from samples of boron phosphate obtained elsewhere (*6*) showed similar line separations. In addition, the lines on the diffraction patterns found with the BPO_4 made in this laboratory were somewhat more diffuse, suggesting that our samples likely are not as crystalline as those prepared elsewhere. It should be noted that the latter samples had been heated to much higher temperatures.

Figure 1 illustrates the essential features of the apparatus employed for the sample handling. The adsorption of water was measured by placing the sample of boron phosphate in a bucket suspended from the end of a calibrated quartz spring with the entire apparatus being enclosed in a glass envelope. Surface areas of the samples were measured by application of the BET theory to data for the adsorption of nitrogen obtained at liquid nitrogen temperature measured in the same apparatus. In order to permit water to be adsorbed on a sample of BPO_4 in the bucket as well as a sample placed on a SEM stub, an arrangement for transferring the stub with the sample to and from the vacuum apparatus and holding it in an upright position in this apparatus, was required. Figure 1 illustrates how this was accomplished with a cylinder of Teflon. For the adsorption of water experiments the tube surrounding the spring and bucket was fitted with a cylinder of Teflon hollowed out sufficiently so as to fit on a finger glassblown to the inside of the bottom of the tube. The SEM stub then sat in a hole drilled in the top of the Teflon cylinder. An additional threaded hole was placed near the upper edge of the cylinder. This permitted a threaded metal rod to be inserted down the glass tube, threaded into the hole in the Teflon, and consequently used to lift the Teflon cylinder with the attached stub out of the glass tube. In an adsorption experiment, sample would be placed on the stub as well as in the bucket so that both would be subjected to the same partial pressure of water vapor. The surface area and the amount of water chemisorbed could be measured with the sample in the bucket and the changes due to various pressures of water vapor could be followed with the sample on the SEM stub.

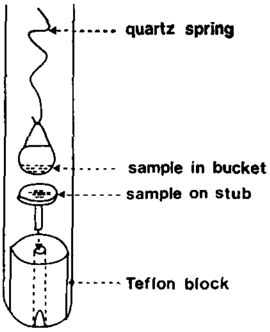


FIG 1. Sample-handling apparatus.

The procedure used is as follows. A sample of boron phosphate was placed in the bucket, the system evacuated to 10^{-6} Torr and an adsorption isotherm for nitrogen at liquid nitrogen temperature was obtained. Scanning electron micrographs were taken of another portion of the same sample which had been sprinkled onto the surface of the SEM stub. Fortunately, it was found unnecessary to coat the sample with gold. The stub was then placed in the Teflon holder and the stub and holder were lowered into the glass tube which was replaced on the apparatus. After careful evacuation of the apparatus to minimize movement of particles, the samples in the bucket and on the stub were exposed to a given pressure of water vapor at room temperature. The amount of water adsorbed by the sample was measured from the extension of the spring. The stub was then removed and the SE micrographs obtained on the sample again. The sample in the bucket was again evacuated and a surface area determined from the adsorption of nitrogen. The SEM stub and its sample were returned to the vacuum system, which was then evacuated to 10^{-6} Torr, and the entire procedure was repeated with a different pressure of water vapor.

To facilitate location of different particles and clusters of particles, a grid was etched on the stub. Regions of study were chosen and insofar as possible, micrographs of each of these were taken after each exposure to water vapor. In preliminary experiments, a portion of the solid sample remaining in the bucket of the spring was transferred to the SEM stub after each water adsorption. However, comparisons of the results of water treatment were then quite difficult. The insertion of the stub and sample into the adsorption chamber with the remainder of the sample circumvented this difficulty at least partially. However, it is then necessary to assume that the sample on the stub adsorbs (per unit of area or mass) the same quantity of water as that in the bucket where the measurement is actually made. Further, this technique could not, of course, prevent some movement of particles on the surface of the stub, although by the use of the technique described the surface of the stub could be kept horizontal, and such movement minimized.

3. Results and Discussion

Figures 2–4 show the results of the SEM study. Figure 2 shows a photomicrograph of a sample of boron phosphate which had not been subjected to either thermal treatment or exposure to water. Such untreated samples had surface areas of 5–10 m^2/g in contrast with those given a thermal pretreatment. The absence of sharp edges may readily be seen from the photomicrograph.

Figures 3a and 3b show part of a sample which had not been thermally pretreated and represent the same particles before and after exposure, respectively, to 4 Torr of water vapor with a resultant weight increase of 30 mg water/g of sample. Changes not unlike those which might be expected on fusion may be readily seen. Figure 3c illustrates the result of exposing a sample of boron phosphate to approximately 20 Torr of water vapor. The presence of a layer of solid on the stub and the drastic changes in the form of the solid are readily evident. The highly disordered surface of Fig. 3a has, in Fig. 3c, given way to a surface which is much more regular. Indeed the sample in Fig. 3c produced a negligible BET surface area.

It was interesting to attempt to determine what quantities of water were needed to be adsorbed in order to observe a difference in the appearance of the sample under the scanning electron microscope. Figure 4a is a photomicrograph of a sample of the solid which had been thermally pretreated as discussed earlier, and Figs. 4b and 4c illustrate the appearance of the same sample after each of the exposures recorded

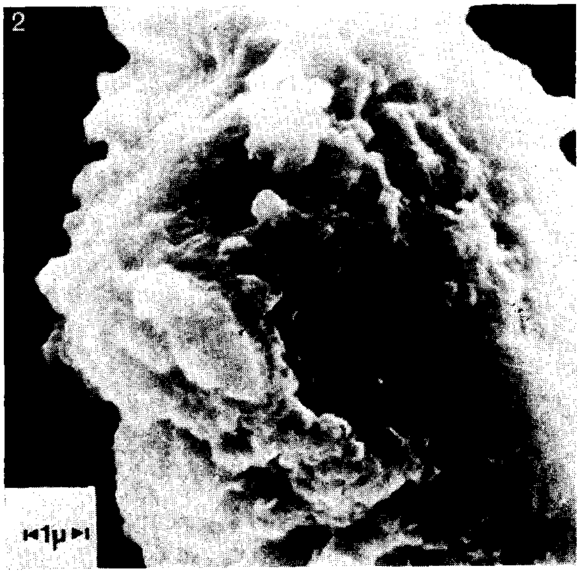
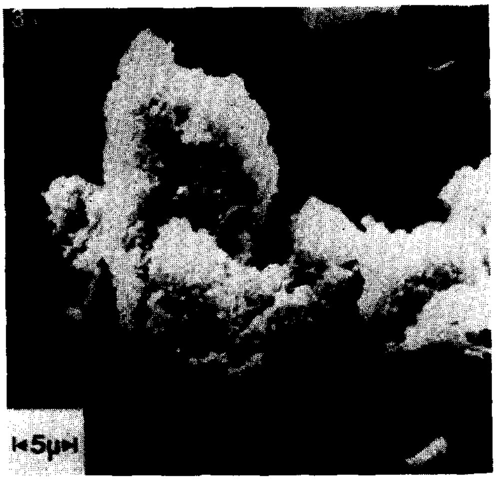


Fig. 2. (11,000×). Untreated boron phosphate.



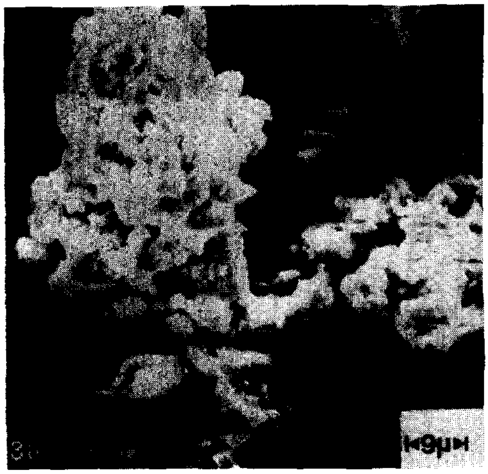


FIG. 3a. (2100×). Untreated boron phosphate.

FIG. 3b. (1050×). Same sample of boron phosphate as in Fig. 3a after exposure to 4 Torr water vapor and weight increase of 30 mg water/g of boron phosphate.

FIG. 3c. (1050×). A sample of boron phosphate which has been exposed to 20 Torr of water vapor.

in Table 1. Although the vapor pressure of water employed here is much less than in the case of that shown in Fig. 3c, so that such pronounced changes would not be anticipated, nevertheless some effects of the water vapor can be observed here. In Figs. 4b and 4c observation of edges perpendicular to the plane of the paper (for example, see arrow) does suggest a "smoothing" of the small sharp peaks on the surface and a replacement of these with a more even surface. In addition, some of the particles may have become somewhat enlarged although it is difficult to be definite on this point since movement of the particles does occur on occasion in spite of care to avoid this. The formation and growth of spheroidally shaped particles can be observed. Other micrographs not shown here indicated that these did

TABLE 1

Exposure number	Water adsorbed (mg/g BPO_4[a])	Surface area after exposure (m²/g)
0	0	27.2
1	30.7	22.7
2	45.4	22.2

[a] Samples were subjected to evacuation at 400°C.

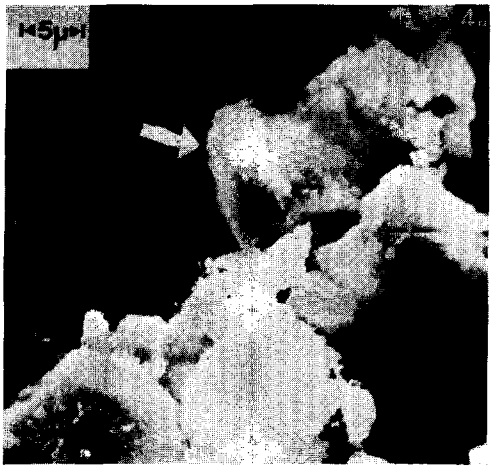


FIG. 4a. (2100×). Unexposed sample of boron phosphate, previously evacuated at 400°C for 8 hr. BET surface area 27.2 m^2/g.

FIG. 4b. (2200×). Same sample as in Fig. 4a after exposure to water vapor at approximately 4 Torr. Surface area 22.7 m^2/g. 30.7 mg water adsorbed/g of sample.

FIG. 4c. (2200×). Same sample as in Fig. 4b after exposure to water vapor (4 Torr). BET surface area 22.2 m^2/g. 45.4 mg water adsorbed/g sample.

not form until the second exposure to water vapor and subsequently continued to enlarge with each exposure to water vapor.

The substantial difference in surface areas between the samples which had been thermally pretreated (in vacuum) and those which had not can probably be attributed in part to a "popcorn" effect as the water is removed from the solid by the treatment and pores and volcano-like structures are created. In addition the photomicrographs suggest that sharp outgrowths from particles will also contribute to such increase in surface area. The 20–25% decrease in surface area of the samples on exposure to relatively small amounts of water would be anticipated to result from a loss of area due to the surface growths rather than a massive change in particle shape or structure. However, exposure to higher pressures of water vapor (20 Torr) produces substantial changes in shape and structure.

It is presumed that initially molecules of water chemisorb on the surface of the solid, while molecules sorbed subsequently can be considered to suffer physical adsorption. Fifty milligrams of water (cross-sectional area 10 Å^2 per molecule) taken up by a solid of 22 m^2 surface area corresponds to a layer of 7–8 molecules of water on the solid. Then, either through a dissolution or hydrolysis process, the outer layers of the solid are taken up by the water molecules which thereby provide the vehicle imparting mobility to the molecules of the solid near the surface. This results in a reduction in the contribution of the high surface energy outgrowths from the main particles, and also, if the quantity of water is sufficient, can lead to the formation of new spheroidal particles of the solid. Larger quantities of water will be sufficient to cause the migration of larger amounts of the solid and ultimately more drastic changes such as observed with 20 Torr of water vapor.

4. CONCLUSIONS

Some insight into the effect of the adsorption of water on boron phosphate has been obtained from this work. Adsorption of water vapor at small pressures produces relatively small changes in surface area which appear to be caused primarily by smoothing of surfaces, while much larger pressures of water vapor give rise to both surface and bulk effects. Although the limitations of resolution of the SEM prevent the examination of changes at the molecular level, nevertheless the present work suggests that the instrument has a considerable potential in the study of the effect of adsorption on the morphology of solids.

ACKNOWLEDGMENT

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