

The Decomposition of Formic Acid on Boron Phosphate

I. Weight and Surface Area Changes of Boron Phosphate During Heating, and Surface Area Changes During Decomposition of Formic Acid on Boron Phosphate

H. L. GOLTZ AND J. B. MOFFAT*

Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada

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Weight changes of boron phosphate (BPO_4) as a result of thermal treatment *in vacuo* at various temperatures have been measured and surface areas subsequent to such treatment and also following exposure to formic acid have been determined as part of a study of the decomposition of formic acid on boron phosphate. In general, the surface areas of BPO_4 increase with the increasing temperature of thermal treatment. However, following an exposure to decomposing formic acid, BPO_4 suffers a loss in surface area for all reaction temperatures. In general the results agree qualitatively for the two different samples of the catalyst used. Some definite trends do appear and it is suggested that the loss in surface area of BPO_4 during catalysis of the decomposition of formic acid is primarily due to the water, produced as a result of this decomposition, acting as a "sintering agent."

INTRODUCTION

Boron phosphate (BPO_4), a white solid at and well above room temperature, possesses some interesting properties. It has been found to catalyze a number of reactions including those which involve a dehydration step in the process of forming intermediate or final products. Interest in boron phosphate in this laboratory has been primarily concerned with its surface properties and its catalytic abilities in dehydration reactions. For the purpose of studying the latter, it seemed reasonable to select a simple reaction involving dehydration which could be used as a "probe" of the surface. The two simplest molecules, aside from water itself, which can undergo reactions involving the loss of water are formic acid and ethanol. Formic acid is known to decompose in the gas phase by two principal reactions, dehydrogenation and dehydration, to yield carbon dioxide,

hydrogen, carbon monoxide, and water, although formaldehyde may form in small quantities. This, together with the fact that many investigations of the heterogeneous decomposition of formic acid vapor on various catalysts have been reported, suggested that a study of the decomposition of formic acid on boron phosphate would be both relevant and interesting.

The present paper is concerned with the changes in both surface area and weight of the boron phosphate during the thermal treatments before the catalyst was exposed to the formic acid vapor, as well as the surface area changes which took place during the decomposition of formic acid.

BORON PHOSPHATE

Since the work done in various laboratories on boron phosphate has not been summarized in the literature, it seems worthwhile to present a brief review at this time.

* To whom inquiries should be addressed.

The physical appearance of boron phosphate depends to some degree on the method used to prepare it and any treatment to which it is subsequently subjected. It is most often found in the form of a white microcrystalline solid, which may or may not be hygroscopic depending on the way in which it was prepared. Some variations exist in the reported parameters of the solid probably due to the variety of methods used in its preparation.

X-Ray diffraction measurements by Schulze (1) gave bond lengths of 1.56 and 1.44 Å for P–O and B–O, respectively, as well as lattice constants ($a = 4.332 \pm 0.006$, $c = 6.40 \pm 0.008$) and a density of 2.802 g/cm³. He suggested a tetragonal bipyramidal crystal structure where both B³⁺ and P⁵⁺ were tetrahedrally coordinated with oxygen, the indices being 1.595 and 1.601, respectively. Dachille and Glasser (2) obtained values of $a = 4.470$, $c = 9.926$, $z = 3$ and a density of 3.069 g/cm³ from powder diffraction studies on high pressure forms of BPO₄. Mackenzie *et al.* (3), on the other hand, found $a = 7.75$, $c = 9.95$ and $d = 3.05$ for material prepared at 85,000 atmospheres and 1000–1200°C. Studies by Bray *et al.* (4) have shown the structure to be analogous to that of cristobalite, consisting of BO₄ and PO₄ tetrahedrally linked by shared oxygen atoms to form a three-dimensional network. These results are in agreement with those of Schulze (1). Other structural characteristics of boron phosphate have been investigated through the use of infrared spectroscopy. For example Weir and Schroeder (5) and Gesmundo and Lorenzelli (6) correlated the structure and catalytic activity while Dachille and Roy (7) related the primary coordination, atomic number, atomic weights, and ionic charge to the absorption wavelengths for major bands. BPO₄ has been found to be thermally stable to a temperature of 1450°C (8) where it vaporizes without decomposition.

The most common uses of boron phosphate are as an ingredient in making glass and ceramics and as a catalyst for certain chemical reactions. It has been used for

many years in both of these applications. As a catalyst, boron phosphate has been used to carry out such reactions as hydration, dehydration, isomerization, and amination. It has been employed, for example, in the pyrolysis of alkyl vinyl ethers to aliphatic aldehydes (9), the elimination of sulfur from hydrocarbons (10), the polymerization of aliphatic monoolefins (11, 12) and the preparation of nitriles from organic acids and ammonia (13). In addition it has been described as useful in the preparation of toluene from benzene and dimethyl ether (14), the manufacturing of butadiene from 1,3-butanediol (15), the isomerization of straight chain olefins to branched chain olefins in the cracking of motor fuels (16).

In most patent and other literature cited, boron phosphate catalyst has been prepared by heating boric acid powder and 85% orthophosphoric acid for several hours at temperatures ranging from 50 to 110°C. The resulting white mass was then dried and calcined at temperatures up to 1000°C. Recent work (17) has uncovered the probable rate-determining step in this reaction. Other less frequently used methods of preparing the catalyst have also been investigated. Boric acid and phosphoric acid have been suspended in an inert solvent such as xylene or petroleum ether (18, 19) and the water released in the reaction was removed along with the solvent by azeotropic distillation. Gerrard and Griffey (20) reacted triethyl phosphate and boron trichloride at –70°C. Upon heating, ethyl chloride was evolved, leaving the white BPO₄. The addition of P₂O₅ to a B₂O₃ melt at 600–650°C resulted in the production of boron phosphate via an exothermic reaction (21). A method of preparing high surface area catalyst has been employed by a number of workers (22–24). The technique involves the reaction of phosphoric acid with various alkyl orthoborates and subsequent removal of the alkyl alcohol and water.

Much of the work done on boron phosphate has involved the study of the influence of various parameters on its reactivity in a number of reactions. Several publications (17, 25–29) by a group of Italian

workers have been concerned with this aspect of the catalyst. They have studied the effect of such variables as the ratio of P_2O_5 to B_2O_3 in the catalyst, calcining temperature, surface acidity, surface area, pore volume, and reaction temperature on its activity toward the hydration of C_2H_2 and C_2H_4 .

These authors found that the surface acidity increases 17-fold as the ratio (R) of P_2O_5 to B_2O_3 increases from 1.0 to 1.5. The catalytic activity was found to be related to this surface acidity and reached a maximum for $R = 1.25$. The method of preparation had a strong influence on most properties of the catalyst. That prepared by reacting boric and phosphoric acid in an organic solvent had a higher surface acidity and initial reactivity than that made by the direct combination but the efficiency dropped much more rapidly than in the latter case. Increasing the calcining temperature resulted in an increased loss of water and was shown to decrease the surface area and acidity, increase the crystallinity, and increase the stability toward hydrolysis and alcoholysis. The rate of occurrence of the latter process was shown to be indicative of the amount of free B_2O_3 present. An increase in R produced a lower specific area and fine pore volume while an increase in the preparation temperature from 300 to 800°C decreased the surface area and acidity. The highest activity was observed for $R = 1.2$ and a 300°C preparation temperature. An investigation into the loss of activity in the hydration of C_2H_2 indicated that such loss was probably due to poisoning by products and not the reduction of surface acidity. The catalytic activity of BPO_4 was also compared to Celite impregnated with H_3PO_4 . It was found that the former was five times as active toward the hydration of ethylene under similar conditions.

Other workers (30) have also noted the catalytic abilities of solids impregnated by H_3PO_4 toward catalyzing hydration reactions. It seems not unreasonable to assume that the catalytic sites for reaction on this catalyst and BPO_4 are similar since the

two catalysts are related chemically and catalyze similar reactions.

Freidlin and co-workers (31, 32) found that the surface area increases with pretreatment temperature and passes through a maximum at 200°C, after which, it decreases. The acidity of the catalyst (per unit wt) decreased with the temperature of preparation but the acidity per unit surface showed a minimum at 600°C, presumably, because the heating initially closed fine pores, reducing the accessibility of the reagent used. Thermogravimetric analysis showed that the catalyst contains two types of water. The one (approx 8%) is easily removed and the other (about 1.5%) is removed only above 450°C. For calcining temperatures above 800°C, the catalyst was completely dehydrated and deactivated. Reactivation was achieved by heating in a stream of air at 550–600°C. Other references to catalyst regeneration procedures involve heating in air at 400–600°C (15) and heating in an oxygen containing gas at 380°C (16).

Richarz *et al.* (33) found that, in the amination of methanol at 360°C, the catalyst activity decreased sharply for the first 10 hr and then more slowly. At 400°C, they observed little or none of this decrease. A study of the ratio of H_3BO_3 to H_3PO_4 in the catalyst preparation by the same authors indicated that the activity was related to the surface area. The highest rates were observed for a quick dried catalyst.

Previous work carried out in this laboratory (23) on boron phosphate involved, in part, the study of the weight loss on evacuation of BPO_4 prepared from the reaction of triethylborate and phosphoric acid. The weight loss was high for low temperatures but leveled off as the temperature was increased. The surface area measured at the end of each pumping and heating stage displayed a maximum in the range 200–300°C. Studies of the adsorption of ammonia indicated a heat of adsorption of 8.9 kcal mole⁻¹. EPR and diffuse reflectance studies (34, 35) of adsorbed aromatic organic molecules on BPO_4 indicated that

the adsorbed species were similar to those present on alumina, which suggested that the sites consisted of both the Lewis and Bronsted type, with the former probably being in predominance. A study of the adsorption of water (36, 37) showed that the amount of water chemisorbed increased with pretreatment temperature, at least up to 300°C. The heat of adsorption ranged between 12 and 15 kcal mole⁻¹ suggesting that the adsorbed water was probably attached to the surface via two hydrogen bonds. Kinetic data gave an activation energy of 12.5 kcal mole⁻¹ which substantiated this belief.

METHOD

Materials

Formic acid. B.D.H. 99–100% formic acid was further purified by distillation under a pressure of 200 Torr of nitrogen. A complete description of the method will be given in a subsequent paper.

Boron phosphate. Two samples of boron phosphate were prepared for this work by mixing various amounts of orthoboric acid and phosphoric acid together in a stirred glass reactor. Two samples were prepared, one containing a mole ratio of H₃BO₃:H₃PO₃ of 1:1.15 and the other 1:1.30. In practice, the amount of Fisher reagent grade 85% phosphoric acid required to give the desired mole ratio was placed in the reactor, heated to 60°C, and 45 g of powdered Fisher reagent grade orthoboric acid (previously sieved through a 20-mesh screen) was added slowly with stirring. Just prior to the end of the 6-hr period the condenser on the reactor was removed. The final paste was spread over the inner surface of a 2 × 30-in. Pyrex tube and was evacuated for 24 hr at room temperature with a mechanical pump. The white solid was chipped from the tube and stored in tightly sealed stained glass bottles. Prior to use the sample was ground and sieved through a 200-mesh brass sieve. The latter operations were performed in a drybag containing dry nitrogen.

Identification of the white powder as

boron phosphate was based on the comparison between powder X-ray diffraction patterns of the material described here and those of samples prepared by other workers. The line separations observed from X-ray pictures of each of the two catalysts proved to be the same as those obtained using boron phosphate received from Victor Chemical Works, Alfa Inorganics, and Dr. V. Ross of Brown University who kindly supplied samples from her NMR work (4) on BPO₄. Material from the first source has been regarded by other researchers (3, 8) as in fact being this compound.

APPARATUS

Since the present paper deals only with surface area and weight changes of the catalyst, a complete discussion of the apparatus as used for the study of the decomposition of formic acid on BPO₄ will be considered elsewhere (38).

During the pretreatment operations and the reactions themselves, the sample of catalyst remained in a quartz bucket suspended from a Cahn R. G. electrobalance built into an appropriate vacuum system. The output from this instrument was fed to a 1-mV Leeds and Northrup Speedomax G. recorder. The quartz bucket was suspended from one balance arm by a tungsten wire 0.004 in. in diameter. Tare weights composed of pieces of Pyrex glass were placed in a similar quartz bucket suspended from the other balance arm. Blank runs were performed with various pressures of relevant gases and with the sample region at various temperatures to permit a compensation for turbulence and buoyancy effects, and adsorption on the various components.

The balance was calibrated to ±1 μg using NBS circular 547 weights before a new batch of catalyst was placed on the pan for a reaction.

After the part of the vacuum system containing the microbalance (henceforth called the "balance system") had been pumped to a pressure of approximately 10⁻⁶ Torr, air was allowed to enter this system. The "hangdown tube" from the balance, which would surround the quartz

bucket and sample, was then removed and cleaned first with carbon tetrachloride, then washed with hot 3*N* sodium hydroxide solution, and finally rinsed 25 times with deionized water, before drying. The used catalyst from the previous run was removed from the quartz pan, which was cleaned by the use of copious quantities of deionized water and finally dried at 110°C. The pan and tube were replaced on the balance system and were pumped to achieve further drying. After air was again allowed to enter, the microbalance was calibrated.

Sufficient catalyst was placed in the pan to permit about 160 mg to remain after evacuation and heating to the desired pretreatment temperature. After the balance system had been slowly evacuated, a furnace was placed around the hangdown tube and the temperature was increased to the desired value. The system was then left overnight for 12 to 16 hr, following which, the furnace was removed and an adsorption isotherm at liquid nitrogen temperatures was obtained using gaseous nitrogen containing less than 16 ppm of oxygen or water, which was further dried by passing through a trap cooled with liquid nitrogen. Surface areas were calculated by applying the standard BET theory. On completion of the isotherm, the system was evacuated at room temperature and the furnace was replaced around the sample. A known pressure of formic acid vapor was then allowed to contact the catalyst and procedures associated with measurement of the rates of the reaction were followed. These latter procedures will be discussed in detail elsewhere. After 6 hr, the system was evacuated and the surface area, was determined again. In some cases the entire procedure was repeated with the same aliquot of catalyst in the sample pan.

RESULTS AND DISCUSSION

Weight Changes

For all runs except those labeled 28-F and 29-F the pretreatment of the catalyst samples was as described. However, in

these two cases, the samples were heated in air for approximately 9 hr.

The weight (%) lost by the catalyst during the pretreatment is given in Table 1. The data suggest that the amount of weight which is lost depends on the catalyst used and the temperature to which it is heated *in vacuo*, as would be expected. As shown, the weight losses for similarly treated aliquots are quite consistent. Figure 1 shows the average loss in weight (%) for all of the samples plotted versus pretreatment temperature. For both catalysts studied, the loss in weight was found to increase with temperature, again as would be expected. However, several additional features of these curves should be noted. Both catalysts lost nearly as much weight on pumping at 25°C as they did in the subsequent heating to 450°C. It appears likely then that much of the material lost consisted of a relatively volatile component (or components), presumably water.

In the temperature range from 100 to 300°C, the curves for the two catalysts appear to be nearly parallel. This suggests that the material being removed from both catalysts may be similar in nature. Catalysts pumped and heated as described here were found to increase in weight again when exposed to air. For this reason and since the catalyst was prepared in an aqueous media and water is produced in the preparation reaction, it seems reasonable to assume that the material being pumped from both catalysts up to at least 300°C is predominantly water. If this be true, the weight loss profile further suggests that this water is bound to (or in) the two catalysts to varying degrees. This may imply that the chemisorbed water on the surface is held by bonds of varying strength. This feature is quite common among catalysts that have an affinity for water. Of course, the weight loss recorded here may also result, in part, from material escaping from catalyst pores and from the bulk of the material. However, little can be said about these mechanisms from the data available.

The greater weight loss for the catalyst with the higher mole percent of phosphoric

TABLE 1
 CATALYST WEIGHT LOSS ON PRETREATMENT

No. of reaction to follow	Pretreatment temp (°C)	Wt loss on pretreatment (%)	Catalyst BPJ
1-F	100	7.3	1:1.15
2-F	150	8.4	1:1.15
3-F	150	8.0	1:1.15
4-F	150	8.5	1:1.15
6-F	150	8.1	1:1.15
8-F	225		1:1.15
10-F	300	10.9	1:1.15
11-F	300	10.8	1:1.15
	225	9.4	1:1.15
13-F	225	9.6	1:1.15
15-F	225	9.5	1:1.15
17-F-A	225	9.9	1:1.15
	225	9.9	1:1.15
19-F	300	10.9	1:1.15
21-F-A	300	10.8	1:1.15
23-F-A	300	11.0	1:1.15
25-F	375	11.4	1:1.15
27-F	450	12.0	1:1.15
28-F	600	(19.2) 0.13	1:1.15
29-F	1000	(22.0) 0.04	1:1.15
30-F	300	10.8	1:1.15
32-F	300	10.8	1:1.15
34-F	300	10.8	1:1.15
	300	11.3	1:1.15
	25	5.5	1:1.15
36-F	150	11.3	1:1.30
37-F	225	12.9	1:1.30
38-F	300	13.5	1:1.30
39	225	12.3	1:1.30
40	225	12.3	1:1.30
41	225	12.6	1:1.30
42	225	12.5	1:1.30
43	225	12.3	1:1.30
44	225	12.8	1:1.30
45	225	12.5	1:1.30
46	300	13.6	1:1.30
47	375	15.2	1:1.30
48	450	16.5	1:1.30
	25	7.3	1:1.30
49	300	13.4	1:1.30

acid is believed to be related to the higher surface area of this material. It is quite possible that the increased loss of weight results from the water produced on dehydration of the excess phosphoric acid to phosphorus pentoxide.

The increase in the slope of weight loss with temperature observed with the 1:1.30 catalyst between 300 and 450°C appears to

be genuine and is believed to be due to the loss of phosphoric acid from the sample. With this sample of BP and temperatures in this range, minute droplets of a clear liquid formed immediately above the furnace on the inner surface of the hangdown tube of the balance.

The weight loss observed for the catalysts labeled 28-F and 29-F is much larger than

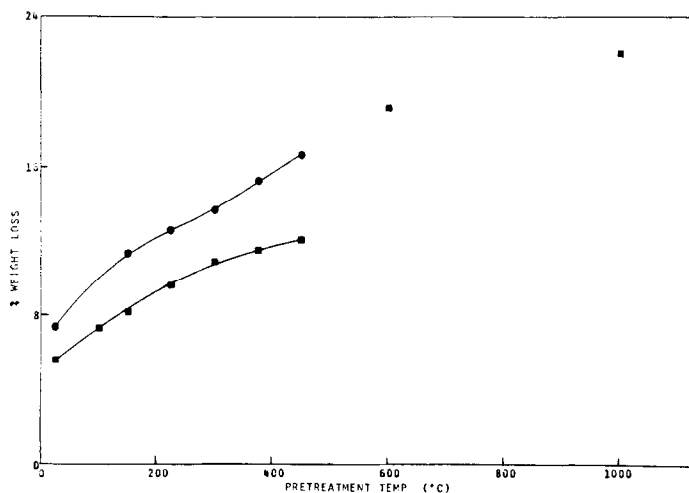


FIG. 1. Percentage of weight lost by the catalysts during pretreatment: (■) BPJ 1:1.15; and (●) BPJ 1:1.30.

would be expected from an extension of the curve obtained for pretreatment *in vacuo* and at lower temperatures. The data in parentheses are those observed while heating in air. The data following the parentheses represent the subsequent weight change when the pretreated catalyst was evacuated and heated to 225°C overnight prior to the reaction. The substantially higher weight losses may be due to loss of B_2O_3 or P_2O_5 themselves or alternatively the loss of orthoboric and/or phosphoric acid formed by the reaction of these oxides with water from the air.

The efficiency with which a material can catalyze a reaction is, at least in part, related to its surface area. Hence, this parameter was studied in some detail in the present work.

Surface Area Variation

As expected, the surface area measured after the catalyst pretreatment, but prior to the first reaction, was found to be altered by the manner in which the pretreatment was carried out. For both catalysts it was found that the surface area was lowered if the sample was not evacuated to approximately 10^{-6} Torr before heating. Aliquots which were not pumped prior to heating are marked with an asterisk in

Table 2 which lists the reaction number in column 1, the F and S standing for first and second reactions on the same aliquot of catalyst. Column 2 indicates which of the two catalysts was used, followed by the reaction temperature and the pretreatment temperature (in parentheses), Columns 4, 5, and 6 of Table 2 list the surface areas obtained after the pretreatment but before the first reaction, before the second reaction, and after the second reaction, respectively. Figures 2 and 3 show part of the data (that which are not marked by a superscript *a*) from Table 2 plotted against pretreatment temperature. The upper line in Figs. 2 and 3 represents the variation in surface area with pretreatment temperature. Points below the top lines represent the surface areas after the first or second reaction. Several pretreatments were performed with no subsequent reaction. These are distinguished by the omission of a reaction number.

As may be clearly seen the initial surface areas are much larger for the 1:1.30 sample than for the 1:1.15 sample. In addition the former material appears to reach a maximum surface area at about 370°C with pumping while that for 1:1.15 continues to increase up to at least 450°C. Up to about 300°C both catalysts have similar area increase profiles with the 1:1.30 sample in-

TABLE 2
 SURFACE AREA MEASUREMENTS

Reaction no.	Catalyst code		Surf. area (m ² /g) and when measured		
	Catalyst used	Temp (°C)	Bef. 1st reaction	Bef. 2nd reaction	Aft. 2nd reaction
1-F	1:1.15	100(100)	16.9 ^a		
2-F	1:1.15	150(150)	19.4 ^a		
3-F	1:1.15	(150)	20.7 ^a		
4-F, 5-S	1:1.15	150(150)	20.6 ^a	13.2	11.9
6-F, 7-S	1:1.15	150(150)	29.7 ^a	16.2	15.7
8-F, 9-S	1:1.15	150(225)	36.3 ^a	15.7	14.8
10-F	1:1.15	150(300)	43.9 ^a	15.7	
11-F, 12-S	1:1.15	150(300)	40.7 ^a	15.7	16.1
	1:1.15	(225)	31.8 ^a		
13-F, 14-S	1:1.15	225(225)	33.8 ^a	19.1	19.3
15-F, 16-S	1:1.15	225(225)	37.0 ^a	20.7	21.2
17-F-A, 18-S-A	1:1.15	225(225)	37.5 ^a	25.2 ^b	22.4 ^c
	1:1.15	(225)	41.2		
19-F, 20-S	1:1.15	225(300)	42.6 ^a	20.9	22.0
21-F-A, 22-S-A	1:1.15	225(300)	24.5 ^a	22.4 ^b	21.8 ^c
23-F-A, 24-S-A	1:1.15	225(300)	47.5	28.2 ^b	23.6 ^c
25-F, 26-S	1:1.15	225(375)	36.5 ^a	22.5	25.9
27-F	1:1.15	225(450)	57.6	30.3	
28-F	1:1.15	225(600)	7.2 ^d	7.7	
29-F	1:1.15	225(1000)	0.0 ^d	0.6	
30-F, 31-S	1:1.15	300(300)	26.2 ^a	26.5	33.0
32-F, 33-S	1:1.15	300(300)	40.0 ^a	29.8	24.9
34-F, 35-S	1:1.15	300(300)	35.5 ^a	30.3	36.2
	1:1.15	(300)	39.7		
	1:1.15	(25)	15.3 ^e		
36-F	1:1.30	150(150)	81.8	34.9	
37-F	1:1.30	150(225)	99.0	38.5	
38-F	1:1.30	150(300)	107.4	45.2	
39-F	1:1.30	225(225)	97.1	19.0	
40-F	1:1.30	225(225)	98.1	18.9	
41-F ^f	1:1.30	225(225)	96.5	18.5	
42-F ^f	1:1.30	225(225)		18.6	
43-F ^g	1:1.30	225(225)		18.0	
44-F ^h	1:1.30	225(225)		15.5	
45-F ⁱ	1:1.30	225(225)		27.3	
46-F	1:1.30	225(300)	109.0	20.3	
47-F	1:1.30	225(375)	111.8	24.0	
48-F	1:1.30	225(450)	104.3	41.3	
	1:1.30	(25)	42.2 ^e		

^a See text for clarification.

^b After 20 min of reaction.

^c After 90 min of reaction.

^d Pretreated in air.

^e Pumped at 25°C, no reaction.

^f Carbon monoxide inhibition run.

^g Water inhibition run.

^h Higher initial formic acid pressure.

ⁱ Lower initial formic acid pressure.

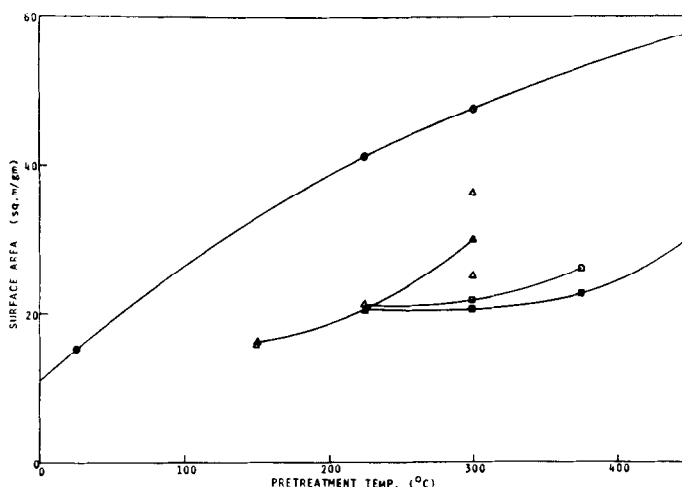


Fig. 2. Surface area trends for BPJ 1:1.15; areas after: (●) pretreatment; (▲) first reaction at 150°C; (■) first reaction at 225°C; (△) second reaction at 150°C; and (□) second reaction at 225°C.

creasing nearly twice as much in surface area per degree as the other sample. It seems not unreasonable to suggest that the decrease in surface area which begins to occur at about 370°C for the 1:1.30 catalyst may be related to the same mechanism which produced the increased weight loss per degree mentioned earlier.

Some indication of the reproducibility of both the surface areas and pretreatment conditions from one aliquot to another may be obtained by examining the areas ob-

tained at the same pretreatment temperatures. For example, runs labeled 37-F, 39-F, 40-F, and 41-F vary by about 1.3%. Because of the consistency of these measurements the areas for runs 42-F to 45-F were taken as the average, $98.0 \pm 1.5 \text{ m}^2 \text{ g}^{-1}$, of the values obtained for the former runs.

Table 2 shows that the surface areas obtained for the two samples pretreated in air at 600 and 1000°C are quite low as compared to those for the catalyst pre-

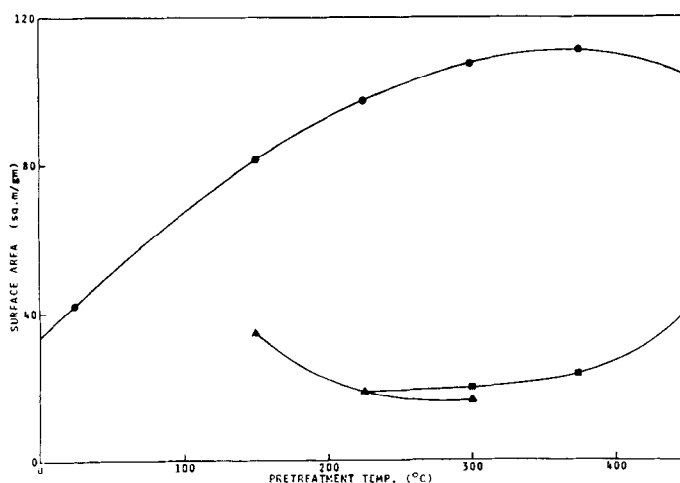


Fig. 3. Surface area trends for BPJ 1:1.30; areas after: (●) pretreatment; (▲) first reaction at 150°C; and (■) first reaction at 225°C.

treated under vacuum at lower temperatures.

With no significant exceptions surface areas were found to have decreased during first reactions. In general, the areas observed after the first reactions appear to be influenced very little by the initial values for similar reaction and pretreatment conditions. For example, surface areas obtained for runs marked 4-F and 6-F, 10-F and 11-F, 13-F and 15-F, and 30-F and 32-F may be compared.

Figures 2 and 3 show that the area profiles for both catalysts as obtained after one 6-hr reaction bear a strong resemblance to each other. In general, little change in the surface area occurs during the second reaction (Fig. 2) but the areas obtained from the 150°C reactions on samples pretreated at 300°C appear to deviate from this general rule. Further, the surface areas obtained after a first reaction appear to be approximately the same for both catalysts for a given reaction and pretreatment temperature. It is interesting to note, however, somewhat in contrast, if the change in surface area for the 1:1.30 catalyst is expressed as a percentage of the original area, the values obtained are nearly the same for a given reaction temperature but different pretreatment temperatures. For example, for reactions with the 1:1.30 catalyst at 150 and 225°C, changes in surface area amount to 59 ± 2 and $80 \pm 2\%$, respectively, for all pretreatment temperatures.

If Figs. 2 and 3 are examined for a particular reaction temperature, it is seen that, in general, the surface area measured subsequent to a first reaction increases with the pretreatment temperature. However, in the case of the 1:1.30 catalyst the surface areas measured following a first reaction at 150°C decrease with pretreatment temperature.

In order to investigate the rate at which the surface area changes during a 6-hr reaction, a number of separate experiments were performed and are labeled with an A in Table 2. It may be seen that most of the decrease in area apparently had occurred after 20 min of reaction and after a second

reaction of 70 min the area was very close to that found after a full 6-hr reaction. This suggests that, for the 1:1.15 sample at least, the surface area decreases quite rapidly during a reaction to a reasonably constant value.

As will be discussed in detail in another paper, formic acid in contact with boron phosphate decomposed almost entirely to carbon monoxide and water. It was found that carbon monoxide did not adsorb in any significant amounts on boron phosphate above room temperature. Hence it must be presumed that the observed decrease in area results from some phenomenon associated with the surface coming into contact with water or formic acid vapor since both of these materials do adsorb. A sample of 1:1.30 pretreated in a similar manner as in runs 39-F to 45-F was exposed to a 2.00 Torr pressure of water vapor for 6 hr at 225°C. The area measured after subsequent pumping at 225°C for 1.5 hr was found to be $18.6 \text{ m}^2 \text{ g}^{-1}$ which agrees quite well with the areas found after the first reactions with 39-F to 44-F. It would thus appear that water vapor was in large part responsible for the observed area decreases during the reactions. However, it is difficult to determine to what extent formic acid may be involved in this process since the formic acid invariably decomposes in the presence of the catalyst.

Thus it seems reasonable to conclude that the loss in weight during preliminary thermal treatment of the BPO_4 catalyst is probably due to loss of water at lower temperatures followed by loss of B_2O_3 and/or P_2O_5 at higher temperatures. Further the increases of surface area with pretreatment temperature can be attributed to this loss of water and the decrease in surface area observed with the 1:1.30 catalyst for pretreatment temperatures above 370°C may then result from the loss of the surplus P_2O_5 at the higher temperature. The loss in surface area of BPO_4 during the catalysis of the decomposition of formic acid can be the result of sintering of the particles with water as the "active agent" in this process. The mechanism of this sintering cannot be

deduced from the information available here but the process may well involve the hydrolysis of boron phosphate itself at the surface of the particles.

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