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Manufacture and Catalytic Activity of Boron Phosphate

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Two kinds of boron phosphate manufacture, which give high acidity catalysts are described. One is based on an excess of H_3PO_4 in the starting mixture of H_3BO_3 and H_3PO_4, the other is based on reacting equimolar amounts of the acids in a boiling organic medium. The catalysts, so obtained, were tested in the gas-phase hydration of ethylene.

As reported in literature, boron phosphate presents a remarkable catalytic activity for a number of reactions. It has been employed as catalyst in dehydration (*1–10*), hydration (*11–18*), polymerization (*19–21*), hydrocarbon conversion (*22, 23*) and desulphurization (*24*), methylation (*25*), isomerization (*26–28*), nitration (*29*), pyrolysis (*30*), organic acids synthesis (*31*), amination (*32, 33*), amides (*34*), and nitriles (*35–38*) manufacture reactions.

Physicochemical properties of boron phosphate, related to its catalytic activity, have been investigated by Freĭdlin *et al.* (*9*), Moffat and Goltz (*39*), Giorgini and Lucchesi (*14*).

Recent studies in our laboratory were carried out on the application of boron phosphate in the catalysis field. Investigations were directed to improve either its activity (*14*) or its manufacture technology (*40, 41*). The present paper reviews results which appeared relevant to this aim.

CATALYST MANUFACTURE

As regards the reactants, boron phosphate has been prepared from: H_3BO_3 and H_3PO_4 (*42, 43*), B_2O_3 and $POCl_3$, BCl_3 and P_2O_5 (*44*), $H_3BO_2F_2$ and PCl_5, PBr_5 or P_2O_5 (*45*), P_2O_5 and molten B_2O_3 (*46*), BCl_3 and $(EtO)_3PO$ (*47*), BP and O_2 (*48–50*). Lately, methods of preparation have been advaced which give catalysts with high surface area (by heating a trialkylborate with H_3PO_4) (*51*) and catalysts with high acidity (by exposing boron phosphate to H_3PO_4 solutions) (*52*).

Our studies have been limited to the manufacture of boron phosphate from H_3BO_3 and H_3PO_4, which reactants were selected from an economical standpoint. Two kinds of boron phosphate, which we denote by BPO_4(a) and BPO_4(b), were prepared.

BPO_4(a). Acidity of catalyst was improved by starting with $H_3BO_3 < 230$ mesh and excess of 85% H_3PO_4, mixing the reactants and keeping the mixture at 100°C up to practically constant weight. The obtained solid was crushed and successively calcined.

BPO_4(b). Spherical particles of boron phosphate have been made by moulding short cylinders of H_3BO_3 and H_3PO_4 mixture into spheres between two plane surfaces, between which there is a relative motion (*53*). An alternative method of granulating, which shuts out the treatment of crushing and the above mechanical processing, was advanced by us. Quasi-spherical particles of boron phosphate were obtained by the following procedure. A flask fitted with stirrer, reflux condenser with water separator, and H_3PO_4 feed funnel was employed. Finely ground orthoboric acid was suspended in xylene and the heating started.

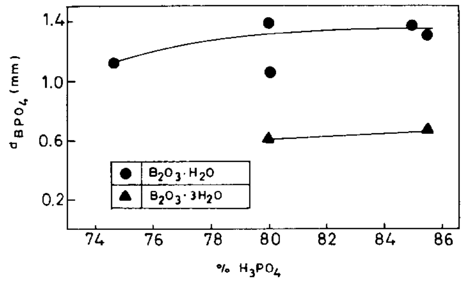

FIG. 1. Weight of mean diameter of BPO_4(b) granules vs. H_3PO_4 weight concentration.

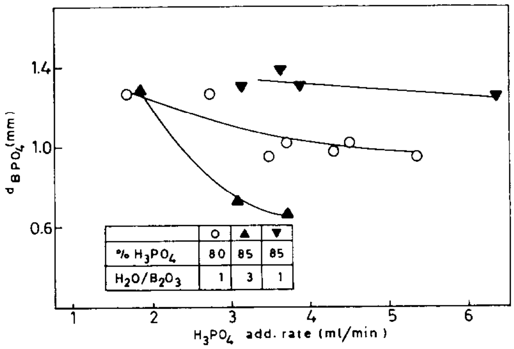

FIG. 3. Weight of mean diameter of BPO_4(b) granules vs. H_3PO_4 addition rate.

At the boiling point of the organic medium, the H_3PO_4 was added at a controlled rate. The water from reaction is eliminated by azeotropic distillation with xylene, which reflows to the flask after water separation. If the addition of H_3PO_4 is delayed, dehydration of orthoboric to metaboric acid occurs (*54, 55*) [dehydration to boron oxide can be achieved by higher boiling point organic media (*56*)], so that the B_2O_3 content of the boric compound may be controlled. The size of BPO_4 granules, which is given as weight of mean diameter, depends on either reactants properties, as H_3PO_4 concentration and B_2O_3 content of boric compound, or processing conditions, as H_3PO_4 addition rate. Figures 1–3 show experiments which were performed in a 3-liter flask with $H_3BO_3 < 230$ mesh and equimolar amounts of reactants corresponding to 0.73 moles of boron phosphate. The observed behavior may be interpreted by picturing the reaction occurring when a drop of H_3PO_4 strikes against a particle of boric acid. In the first steps of reaction, the product is less viscous, the lower the H_3PO_4 concentration or B_2O_3 content of boric compound. It follows, as an effect of agitation, a smaller size of the final granules of boron phosphate. Of course, a less initial viscous product is also obtained with an higher H_3PO_4 addition rate.

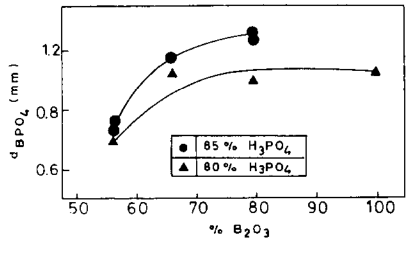

FIG. 2. Weight of mean diameter of BPO_4(b) granules vs. B_2O_3 weight content of boric compound.

CATALYTIC ACTIVITY

The two kinds of boron phosphate above described were employed as catalyst in the gas-phase hydration of ethylene. The catalytic activity was related to the amount of acid sites of catalyst.

The acidity of BPO_4(a) was measured by titrating the solid in anhydrous benzene with 0.1 N n-butylamine in the presence of Hammett indicators (*57, 58*). The indicators used: phenylazonaphthylamine ($pK_a = +4$ to -3), dicinnamalacetone ($pK_a = -3$ to -5.6), benzalacetophenone ($pK_a = -5.6$ to -8.2) and anthraquinone ($pK_a < -8.2$) point out the different acid strength of the acid sites. No acid sites with $pK_a < -8.2$ have been revealed. The strong ($pK_a = -5.6$ to -8.2) and intermediate ($pK_a = -3$ to -5.6) acidity has been measured by the change of color of solid after 5 hr, the weak one ($pK_a = +4$ to -3) after 20 hr. For BPO_4(b), which is a little dark for the presence of organic residual products, the above method was extended by mixing the samples with BPO_4(a) of known acidity (*59*). The acidity of the catalysts with sizes in the range 1.2 to 1.5 mm and calcined 4 hr at 300°C, is illustrated in Table 1. The weak, intermediate, and strong acidity of BPO_4(a) increases with the P_2O_5/B_2O_3 molar ratio in the starting

TABLE 1
Acidity of Boron Phosphate

Catalyst	Acidity $BuNH_3$ (mmoles/g of cat) Phenylazo-naphthylamine $pK_a = +4$ to -3	Dicinnamal-acetone $pK_a = -3$ to -5.6	Benzalaceto-phenone $pK_a = -5.6$ to -8.2	Total
BPO_4(a)				
P_2O_5/B_2O_3 = 1.0	0.03	0.15	0.12	0.30
1.1	0.67	0.97	0.29	1.93
1.2	1.10	1.47	0.83	3.40
1.3	1.62	1.77	1.06	4.45
1.5	1.65	2.17	1.21	5.03
BPO_4(b) from				
$B_2O_3 \cdot H_2O$	1.10	1.02	0.69	2.81
$B_2O_3 \cdot 3H_2O$	0.95	0.27	0.04	1.26

mixture of reactants and BPO_4(b) prepared from metaboric acid results more acid than BPO_4(b) prepared from orthoboric acid. Both BPO_4(b), which were manufactured using equimolar amounts of reactants ($P_2O_5/B_2O_3 = 1.0$), are more acid compared with the corresponding BPO_4(a), which has the same initial P_2O_5/B_2O_3 molar ratio.

The catalytic activity was tested in a fixed bed differential reactor at 300°C, fed with ethylene–steam mixture from an evaporator in the molar ratio of 1:1.5 at atmospheric pressure. BPO_4(a) and BPO_4(b), with sizes in the range 1.2 to 1.5 m, have been previously calcined 4 hr at 300°C. The gas mixture from the reactor was condensed and the solution was analyzed by a gas chromatograph (Carlo Erba Model C apparatus equipped with thermal conductivity detector), where ethyl alcohol and water could be determined. A 2-m column of 20% Carbowax 1500 on Teflon was used. The column was kept at 120°C and the rate of helium gas flow, as a carrier gas, was about 3 liters/hr.

Cracking reactions, which are likewise catalyzed by acid catalysts, occur to some extent, causing deactivation of boron phosphate due to carbon deposits. Further deactivation may be ascribed to the loss of phosphoric and boric components from the catalyst, which alters the active surface (*6, 14*). The weight loss of catalyst after 50 hr (the age is measured from the time the boron phosphate is put into contact with the reaction mixture) is reported in Table 2; the loss of catalyst, analogously to the fouling, increases with its acidity.

TABLE 2
Weight Loss of Catalyst After 50 hr

Catalyst	Wt loss (%)
BPO_4(a)	
P_2O_5/B_2O_3 = 1.0	3.91
1.2	9.78
1.5	12.24
BPO_4(b) from	
$B_2O_3 \cdot H_2O$	5.14
$B_2O_3 \cdot 3H_2O$	6.83

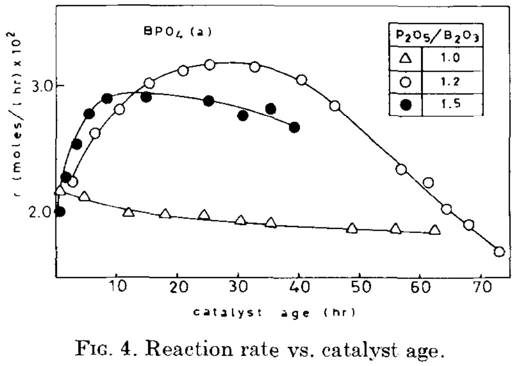

Fig. 4. Reaction rate vs. catalyst age.

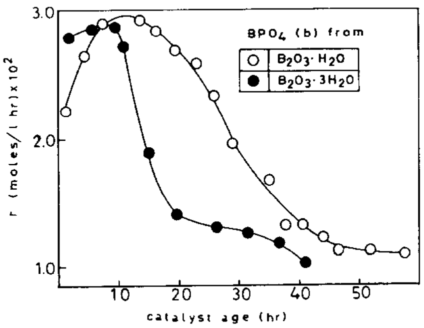

FIG. 5. Reaction rate vs. catalyst age.

The results of ethylene hydration are given by the reaction rate, *r*, which is defined as ethylene moles converted to ethyl alcohol per hour and liter of catalyst pellets. The reaction rate, as visualized in Figs. 4 and 5, which represent 3 and 2 runs, respectively, varies with the age of the catalyst, and after a maximum value, it decreases owing to the catalyst poisoning. The maximum catalytic activity of BPO_4(a), diagrammed in Fig. 6, increases sharply, in the range 0.8 to 1.2, with the P_2O_5/B_2O_3 molar ratio. With higher values of the ratio, the reaction rate decreases. The same behavior has occurred in high pressure hydrations (*15*). Compared to the maximum value achieved by the reaction rate, BPO_4(b) results are more active compared with the corresponding BPO_4(a), but its activity decreases sooner.

It is plain that high catalytic activities are obtained with catalysts having initial high acidities, to which, therefore, we may ascribe the catalytic behavior of boron phosphate in the ethylene hydration. Nevertheless, the more acid the catalyst, the more rapid its deactivation results, so that a further increase of acidity in very acid catalysts may mask a likely corresponding increase of activity, lowering the maximum reaction rate observed. This occurrence may be supposed for BPO_4(a), when the P_2O_5/B_2O_3 molar ratio is higher than 1.2.

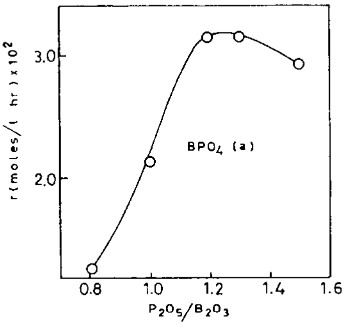

FIG. 6. Maximum reaction rate vs. P_2O_5/B_2O_3 molar ratio in the mixture of reactants.

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