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Catalytic Activity and Selectivity of Boron Phosphate in the Decomposition of Ethyl Alcohol Vapor

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The decomposition of ethanol over boron phosphate has been studied from 255 to 370°C. Ethylene and diethyl ether are the only significant products. The percent conversion to ethylene is a continuously increasing function of temperature while that to ether passes through a maximum at approximately 300°C.

INTRODUCTION

The heterogeneous decomposition of ethanol vapor has been widely studied (*1*) as a means of investigating the properties of catalytic solids, and particularly those capable of catalyzing dehydration reactions. Since ethanol decomposes primarily to ethylene and/or diethyl ether, this reaction can serve as a probe for both catalytic activity and selectivity.

Surface and catalytic studies in this laboratory (*2*) have been largely concerned with boron phosphate, particularly in respect to its properties as a dehydration catalyst. As part of our program to examine the dehydration of simple molecules on boron phosphate, studies of the decomposition of ethanol were initiated. However, as will be discussed later, problems with the analytical method prevented the determination of accurate kinetic data, and consequently ethanol has been abandoned in favor of other alcohols. Although the accuracy of the present data does not warrant calculations of rate constants, nevertheless it is believed desirable to report on the primary data in order to demonstrate, at least semiquantitatively, how the catalyst and reaction itself behave as a result of variation of a number of parameters. The composition of the product vapors was measured in a flow apparatus and hence the selectivity and percent conversion were obtained as a function of reaction temperature (255-370°C) and pretreatment temperature of the catalyst.

METHOD

Boron phosphate was prepared from a 1:1.12 molar ratio of boric to orthophosphoric acid. The boric acid and orthophosphoric acid were of Fisher Certified A.C.S. grade and Baker Analyzed (86%) grade, respectively. These were heated together at 25-40°C for 6-8 hr and the result was dried at 150°C, ground, and sieved through 100 mesh. The fines were stored in screw-cap vials and were subjected to evacuation and heating at temperatures of 300, 400, and 500°C prior to use.

The apparatus used will be described in detail elsewhere (*3*). A helium stream of controlled flow rate was passed through an ethanol saturator held at a fixed temperature. The helium passed over the catalyst held in a stainless-steel mesh basket in a tubular furnace whose temperature was measured with a chromel-alumel thermocouple. The exit stream was sampled by means of a variable leak valve attached to a CEC mass spectrometer. Steady reaction conditions were attained in the differential reactor after 3-8 hr, depending on reaction temperature. For each reaction temperature analyses were made for four successively increasing flow rates of helium, corresponding to decreasing contact times.

Results and Discussion

Figure 1 illustrates the products obtained as a function of reaction temperature. It is readily observed that boron phosphate catalyzes the decomposition of ethanol to diethyl ether and ethylene. No other products were found in significant quantities. Blank runs of ethanol vapor on the reaction system did not produce measurable quantities of either products at any temperatures used in this work. The figure indicates that the relative amounts of diethyl ether and ethylene are a function of the reaction temperature. The yield of ethylene (expressed as mole percent of the product) increases continuously with temperature in the range studied while the yield of ether passes through a maximum at 290–300°C. Up to at least 340°C, the yields are not a function of the pretreatment temperature of the catalyst. In all of this work the mass balances were 100 ± 10%. Since the surface areas (BET nitrogen) of the catalysts were essentially independent of pretreatment temperature, the results given in the figure may be interpreted as obtained at similar total surface areas. Surface areas before and after the reaction were 28–31 m^2 g^{-1} and 25–29 m^2 g^{-1}, respectively.

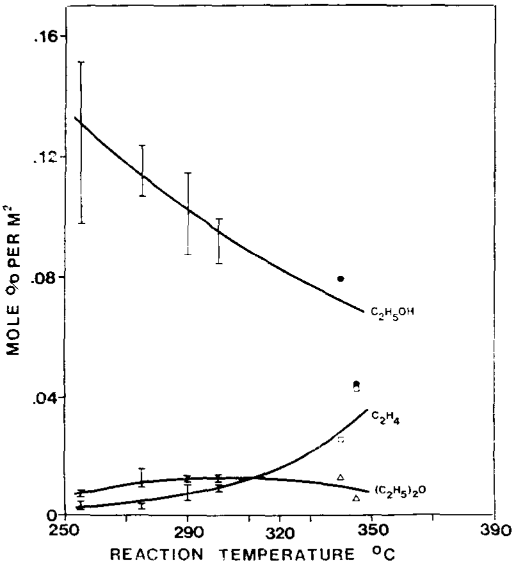

Fig. 1. Products from the decomposition of ethanol over boron phosphate at various temperatures. Ethanol ●; diethyl ether △; ethylene □.

The contact time dependence of product formation is shown in Fig. 2 for reaction temperatures of 290 and 345°C. At 290°C, a higher conversion to diethyl ether occurs while at 345°C, the ethylene predominates.

An additional experiment on a catalyst pretreated at 400°C and reaction temperature of 370°C produced a conversion of 75% after 13 hr but only 54% after 30 hr. Considerable deactivation of the catalyst was further evidenced by its black color at the conclusion of the test. After 13 hr at 370°C the vapor consisted of 0.0262, 0.0581, and 0.0009 mole% per square meter of ethanol, ethylene, and ether, respectively. After 30 hr of the same experiment, the concentration of ethanol had increased to 0.0602, that of ethylene had decreased to 0.0394, and that of ether had increased to

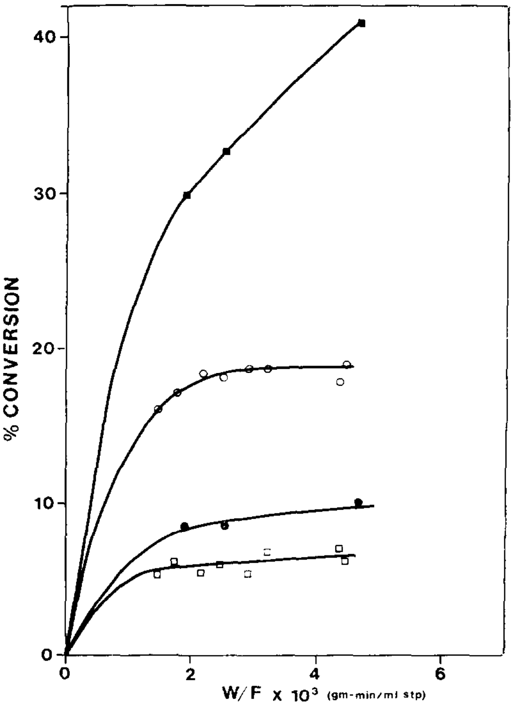

Fig. 2. Contact time dependence of product formation at 290 and 345°C.

	290°C	345°C
diethyl ether	○	●
ethylene	□	■

0.0026 mole% per square meter of catalyst surface.

The addition of either ethylene (34.2 Torr) or diethyl ether (194.6 Torr) to the reactant gas stream containing ethanol (at partial pressures of 47.2 and 50.4 Torr, respectively) appeared to have little or no effect on the reaction at 275°C. However, the addition of quantities of water (of partial pressure less than 20.4 Torr) decreased the rate of production of ether by approximately 40% while having no effect on the rate of production of ethylene (275°C reaction temperature).

Unfortunately, as indicated in the introduction, and as is evidenced from the error bars in Fig. 1, the analytical method is subject to considerable uncertainty at very low conversions. Although this uncertainty is reduced as the conversion increases, the kinetic data obtained in the region suitable for differential reactor treatment display substantial scatter and for this reason are not reported here.

It is interesting to note that ΔG is negative for the decomposition of ethanol to ethylene at all temperatures used in this work, whereas the decomposition to diethyl ether has a negative ΔG up to approximately 287°C. This is approximately the temperature at which the maximum in the yield of ether is attained (Fig. 1).

Presumably the ethylene and diethyl ether are produced by simultaneous competing processes at 290°C and lower temperatures, while at temperatures of 340°C (Fig. 2) and higher, either more of the ethanol is initially dehydrated to ethylene or alternatively the ether produced is successively dehydrated to ethylene.

It is interesting to compare the present results with those on other, somewhat similar catalysts. Since boron phosphate $(BPO_4)_2$ can be thought of as $B_2O_3 \cdot P_2O_5$, some analogy to alumina and silica–alumina catalysts can be drawn. Kibby and Hall (*4*) have recently stressed the relationship between alumina and hydroxyapatite (calcium phosphate) surfaces. Since alcohol dehydration on alumina is well known it is not unexpected that boron phosphate would catalyze the dehydration of ethanol. With hydroxyapatite some dehydrogenation of the alcohol also occurs but above 300°C, the major reaction is dehydration. As Kibby and Hall point out, although the dehydration of simple aliphatic alcohols is thermodynamically favorable at temperatures above 100°C, the activation energies are approximately 60 kcal $mole^{-1}$ in the gas phase, thereby rendering the uncatalyzed dehydration ineffective below 500°C (*5*). It is interesting to note that over alumina the decomposition of alcohols often produces an ether as well as an olefin. However, in the case of hydroxyapatite such is not the case, only the olefin being found to form. This suggests that the surface of boron phosphate may be more similar to that of alumina or silica alumina than to that of calcium phosphate. Kibby and Hall (*4*) attribute the difference in behavior of alumina and hydroxyapatite to a lack of Brönsted acidity on the surface of the former. The surface of alumina may consist of bridged oxygen (surface anhydride) groups which leave alcohols to form OR and OH groups so that OR (alkoxide) groups adjacent to one another may desorb as an ether.

In the case of the boron phosphate used in the present work it is presumed that a sufficient excess of phosphorus is present to provide for an ample number of Brönsted sites, although previous work from this laboratory (*6*) suggests that the number of Lewis acid sites on boron phosphate is much larger than those of the Brönsted type. It is tempting to speculate that the absence of measurable quantities of ether in the case of hydroxyapatite might in part be due to a higher catalytic activity for the decomposition of the ether to the olefin. However, the difference in behavior of boron and calcium phosphates in respect to decomposition of ethanol must be considered as yet unresolved.

Some comparison of the present results with those obtained for the decomposition of ethanol on less similar catalysts is worthwhile. Mochida, Kato, and Sliyama (*7*) found that the decomposition of ethanol at 300°C over metal sulphates produced both ethylene and diethyl ether and the variation of % conversion with contact time obtained by them is quite similar to that reported here. Although the analogy with alumina must be carefully made, infrared studies (*8*) of diethyl ether adsorbed on dehydrated alumina show the presence of a coordination complex, $(C_2H_5)_2O\text{–}Al<$ below 100°C and a surface ethoxide, $C_2H_5O\text{–}Al<$ above 100°C. Thermal decomposition of the former below 130°C produced a mixture of ethanol, diethyl ether, and ethylene, while above 130°C ethylene was primarily produced, as was the case with the decomposition of the surface ethoxide at 210°C. Bennett and Ross (*9*) found varying amounts of acetaldehyde as well as both ether and ethylene when the decomposition of ethanol was measured over alumina–spinel oxides in the range of 360–480°C. All their catalysts produced ethylene but only those containing octahedrally coordinated aluminum produced diethyl ether, while acetaldehyde was not found in products from catalysts with only tetrahedrally coordinated aluminum. Finally, it has recently been proposed (*10*) that the dehydration of ethanol on alumina can be satisfactorily explained by a reaction mechanism involving adsorption of the alcohol molecules on two types of active sites, one basic and the other acidic, and a subsequent reaction between an adsorbed ROH molecule on an acidic site and an adsorbed alkoxide anion on a basic site.

In summary, it has been shown that boron phosphate catalyzes the decomposition of ethanol to ethylene and diethyl ether, the conversion to ethylene being a continuously increasing function of temperature while that to ether passes through a maximum at about 300°C. Below 310°C the product is mostly ether while above 310°C it is primarily ethylene. At temperatures below 310°C the percent conversion to both products approaches a constant value with increasing contact time while above 310°C that of ethylene appears to be continuously increasing. The evidence appears to suggest simultaneous dehydration to the two products, with the reaction producing ethylene dominating at temperatures above 310°C.

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