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The Decomposition of 1-Propanol Vapor on Boron Phosphate

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The decomposition of *n*-propanol catalyzed by boron phosphate prepared from *ortho*-phosphoric and boric acids in molar ratios varying from 1.0/1.0 to 1.5/1.0 has been studied in the temperature range 170–205°C, and the products were propylene and water. The data were found to fit the Langmuir–Hinshelwood theory, and rate constants (0.0077 to 0.074 ml (STP) min^{-1} m^{-2}), activation energies (14.9 to 29.6 kcal $mole^{-1}$), and apparent heats of adsorption of *n*-propanol (-6.0 to -25.8 kcal $mole^{-1}$) all were found to depend on catalyst composition and pretreatment temperature. A correlation with total surface acidic concentration is proposed.

INTRODUCTION

Studies of the decomposition of relatively small molecules on solids provide useful information concerning the catalytic properties of the surface of the solids. One such molecule whose decomposition has been examined with a wide variety of catalytic solids is ethanol, and in this laboratory such decomposition has provided further information on the catalytic properties of boron phosphate (*1*). It was found that ethylene and diethyl ether are the only significant products of the decomposition of ethyl alcohol vapor over boron phosphate (BPO_4) from 255 to 370°C, with the percentage conversion to ethylene being a continuously increasing function of temperature while that to ether passes through a maximum at approximately 300°C.

Infrared spectroscopic studies (*2*, *3*) of boron phosphate and adsorbed species have demonstrated the presence of BOH and POH, among other structures, and an essentially reversible desorption and adsorption of water, which was partially dissociated on adsorption. On adsorption of ammonia, dissociation appears to occur, and bands assignable to coordinately bonded ammonia and to NH_4^+ were observed. Such studies therefore provide support for the previous contention (*4*) of the existence of both Brønsted and Lewis acid sites on the surface of boron phosphate. As suggested at that time, one might therefore anticipate some similarity between silica–alumina and boron phosphate.

As a means of providing further information on the catalytic properties of boron phosphate and to extend our earlier work on ethanol decomposition, the decomposition of 1-propanol vapor over this catalyst was studied.

METHOD

Four different samples of catalyst were prepared by mixing boric acid (powdered Fisher reagent grade) and *ortho*-phosphoric acid (Fisher reagent grade 85%) in various ratios for 5 hr at 38–39°C. The mixture was then heated in air at 150°C for 24 hr and at 350°C for a further 12–14 hr. After cooling in a sealed container, the catalyst was ground, sieved through 100 mesh, and stored as 1-g samples in tightly sealed glass vials. A fresh sample of catalyst from a previously unopened vial was employed for each reaction described later.

The 1-propanol was the middle, constant-boiling fraction (95.4–95.6°C at 740.8 Torr) of distilled Baker analyzed reagent grade. The refractive index of this fraction was measured as 1.3832 at 25.5°C (literature, 1.3832–1.3835, 25°C). Propylene was Matheson research grade gas (minimum purity 99%) and di-*n*-propyl ether was Matheson, Coleman and Bell "highest purity," both being used as received. Helium and nitrogen gases (marked minimum purity 99.995%) were obtained from Union Carbide.

Prior to use in a reaction, each sample of catalyst was pretreated at 311°C for 16–17 hr, or 421°C for 10–11 hr, or 536°C for 10–11 hr, all at 10^{-5} to 10^{-6} Torr. Such periods of time were sufficient to produce a constant surface area at the given temperature. BET nitrogen surface areas were measured at liquid nitrogen temperatures both before and after each reaction using a Cahn R-G electrobalance combined with a Quartz Precision pressure gauge (Texas Instruments Model 141 with 0–10 psi capsule).

The decomposition was measured in a flow apparatus in which a regulated flow of helium carrier gas was saturated at a known temperature with the alcohol and this gaseous mixture, which could be diluted by a second stream of helium, was passed through a bed of boron phosphate. The apparatus employed standard glass vacuum stopcocks except where the system came in contact with either reactants or reaction products, in which case Teflon grease-free stopcocks were used. The flow of carrier gas was controlled by a Brooks Instrument (Model 8744) flow controller and was measured by two flowmeters, one a Brooks Sho-Rate flowmeter, the other, a soap-bubble type. Both the stream of helium to be saturated and that employed as dilutant were fitted with these devices together with drying tubes.

The stream of helium was saturated with the alcohol by first passing it through an evaporator held at 32°C and containing the alcohol and subsequently through a condenser held at various temperatures between 21 and 23°C (±0.1°C.). The helium was assumed to be saturated with alcohol at the temperature of the condenser as liquid alcohol continually collected there. In addition, the partial pressure of alcohol was found to be constant to ±1% over a considerable range of flow rates, thus confirming saturation and also indicating no supersaturation. The partial pressure of alcohol in the gas stream was assumed to be the vapor pressure at the temperature of the condenser.

The tube reactor consisted of an inner tube through which the gases travelled prior to passing through the catalyst held in a pan made from stainless-steel screening. The gases passed out of the reactor via the outer tube which fit the inner diameter of the Marshall tube furnace and was attached to the inner tube by means of Cajon ultra-Torr unions. The temperature of the furnace was controlled to ±1°C and measured with a calibrated chromel–alumel thermocouple.

The exit gases were sampled by means of a variable leak valve (Granville-Phillips Co. Automatic Pressure Controller Series 213) controlled by an ionization gauge (Consolidated Vacuum Corp.) with detecting head at the inlet port of the analyzer tube of a mass spectrometer. The mass spectrometer was calibrated by sampling from the helium stream (bypassing the reactor) containing known partial pressures of 1-propanol. With propylene–helium mixtures, known flow rates of propylene were added to the helium. In all cases total pressures were measured. A given peak height registered by the mass spectrometer was found to be sensitive to both the amount of the particular species present and the total pressure. Since, even with the variable leak valve operating, there is still some oscillation in pressure within the mass spectrometer, ratios of peak heights rather than absolute peak heights were found and were related to ratios of partial pressures. For 1-propanol the *m/e* peaks monitored were 41, 31, 4, and the ratios 31/4 and 41/31 were considered, while for propylene the 41 and 4 peaks and the ratio 41/4 were followed. Appropriate corrections for the contribution of propanol to the 41 *m/e* peak were applied. The calibrations of the mass spectrometer were checked frequently during the course of this work. By analysis of text mixtures of known composition it was found that the present method of analysis was accurate to less than ±1.5% and reproducible to less than ±1%.

RESULTS AND DISCUSSION

Five different catalyst compositions (Table 1) were prepared and were used in various catalyst characterization experiments. It was found that the surface areas of the boron phosphate samples prior to pretreatment were a function of the phosphoric to boric acid ratio (Table 1). As has been found previously in this laboratory, the surface area also increases on pretreatment. The durations of the pretreatments at the various temperatures are given in the experimental section. Such times were selected to be sufficiently long to ensure that a constant surface area was reached for each particular pretreatment temperature. Table 2 shows an example of the effect of pretreatment temperature and duration of pretreatment on the surface area of one catalyst sample. Similar results were obtained for the other samples. At the lowest pretreatment temperature (311°C) the surface area increased with time up to approximately 14 hr while at the higher pretreatment temperatures (421 and 536°C) constant surface area was achieved in 6 hr or less. As can be seen from Table 2 the ultimate constant surface areas are approximately the same for each pretreatment temperature.

TABLE 1

Compositions and Surface Areas (No Pretreatment) of Samples of Boron Phosphate

Label	H_3BO_3/H_3PO_4 (molar)	Initial surface area ($m^2\ g^{-1}$)
BPR-3	1:1.01	23.07
BPR-2	1:1.11	18.32
BPRS-2	1:1.12	14.96
BPR-1	1:1.30	8.33
BPR-4	1:1.51	—

TABLE 2

Surface Area at Various Pretreatment Times and Temperatures[a]

Time (hr)	Surface area ($m^2\ g^{-1}$) at pretreatment temperature		
	311°C	421°C	536°C
0	14.96	14.96	14.96
3		31.68	
6	25.54	29.82	29.68
9	29.20		
12		31.51	
14	32.03		
15			30.61
18	31.81		
24	31.35	29.18	29.53
40	32.03		
53		32.65	

[a] Catalyst sample BPRS-2: H_3BO_3/H_3PO_4 = 1:1.12.

As has been mentioned in the experimental section, surface areas of samples were measured both before and after each reaction and were found to decrease after reaction. The average such loss of surface area was 10%. Such losses are much smaller than found previously in studies of formic acid decomposition in a static reaction system (*5*) where surface area decreases as high as 80% were observed. It is presumed that such losses both in the previous and present work are due to the presence of water vapor, the losses being smaller in the more recent work as a consequence of the use of a flow reaction system which assists in maintaining the partial pressure of water vapor in the vicinity of the catalyst at a lower level than that in a static system. Previous work in this laboratory demonstrated the deleterious effect of water vapor on the surface area of boron phosphate (*6–8*).

Decomposition reactions were carried out at the same four temperatures for each of the three pretreatment temperatures and for each of three catalyst compositions. In some cases, more than one run was made under a given set of conditions in order to check the reproducibility. As has been mentioned, a fresh aliquot was used for each reaction. The only products of the decomposition of 1-propanol on boron phosphate that were detected in measurable quantities were propylene and water. Preliminary experiments showed that it would be necessary to study the decomposition in the temperature range 170–205°C, in order to operate the reactor under differential conditions. Experiments with 1-propanol at these reaction temperatures, in the absence of a catalyst, showed no evidence of decomposition.

Since in all reactions, conversions were low, no problems were encountered in achieving steady-state conditions. However, in order to investigate the possibility of catalyst deactivation during a reaction, a test experiment was performed in which a constant partial pressure of 1-propanol was passed over a sample of catalyst at 185°C for 36 hr. Steady-state conditions were attained after approximately 10 hr and maintained, within experimental error, for the duration of the experiment.

In the present work the rate of formation of propylene was taken as a measure of the rate of reaction. To determine the extent to which propylene might be retained in a chemisorbed form on the catalyst, the increase in weight of a sample of the catalyst held at 196°C and exposed to 5.4 Torr of propylene was measured in a Cahn balance vacuum system, over a period of 18.5 hr. This temperature is within the range of temperatures used to study the decompositions of *n*-propanol in the flow system. The pressure of 5.4 Torr is greater than the maximum partial pressure of propylene attained during any of the reactions. At the end of the adsorption period, the weight adsorbed corresponded to a coverage of approximately 4% of the available surface and represented less than 0.1% of the propylene produced in the same time during any of the reactions. It was concluded that all but negligible amounts of the propylene produced in a reaction is present in the product vapors, and hence the rate of production of propylene could be considered to be an indication of the rate of reaction.

The partial pressures of both 1-propanol and propylene were measured at various time intervals. The relative ease of attainment of steady-state conditions for both these constituents with the present system suggested either that adsorption on the system walls was negligible or that adsorption equilibrium was rapidly attained. Initially, attempts were made to calibrate the mass spectrometer for water and to follow its partial pressure during the reaction. This was unsuccessful but mass balances of 100 ± 5% were obtained for all reactions from the use of stoichiometric values for water and measured pressures for propanol and propylene. The rate of formation of propylene was related to the average of the partial pressures of 1-propanol in the gas streams entering and leaving the reactor in a given experiment.

A number of experiments were performed to estimate the importance of diffusional effects. Reactions were carried out at 185°C on catalyst BPR-1 pretreated at 421°C with a variety of weights of catalyst. The rate of reaction per unit surface area was found to be constant, within experimental error, in all cases. Experiments in which the flow rate of propanol through the reactor was varied, with the partial pressure of the alcohol being held constant, showed that constant rates of reaction could be obtained in a range of ±35% of the flow rate used in the experiments. As a further check of diffusional effects, the method described by Smith (*9*) was employed to estimate the difference between the partial pressures of 1-propanol in the bulk stream and at the surface of the catalyst. The Reynolds numbers were estimated to be in the range of 0.01 to 0.02, indicating a partial pressure difference of less than 2% for all the reactions carried out. On the basis of these tests it was assumed that diffusional control did not exist.

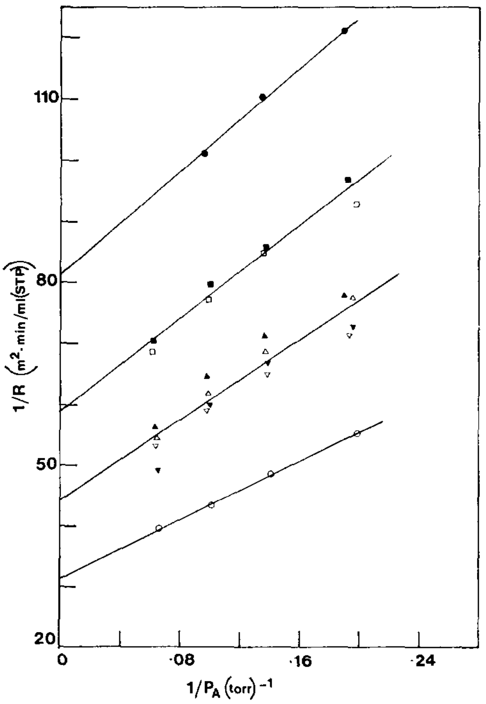

FIG. 1. Langmuir–Hinshelwood plot for reactions on BPR-1 (boric:phosphoric = 1:1.30) pretreated at 421°C. The symbols indicate the following reaction temperatures and reaction numbers: (●), 170°C, 1; (■), 175°C, 1; (□), 175°C, 2; (▼), 185°C, 1; (▲), 185°C, 2; (▽), 185°C, 3; (△), 185°C, 10; (○), 195°C, 3.

In all cases the data were fitted to an equation of the form

$$R = kKP_A/(1 + KP_A),$$

where R is the rate of production of propylene (ml STP m^{-2} min^{-1}), P_A is the average partial pressure of 1-propanol in the reactor (Torr), and K and k are constants. If the reaction is assumed to follow a Langmuir–Hinshelwood mechanism, then K is the equilibrium constant for the adsorption of 1-propanol and k is the unimolecular first-order rate constant for the decomposition of the 1-propanol adsorbed on the surface of the catalyst. Figure 1 shows a plot of $1/R$ versus $1/P_A$ for BPR-1 (boric:phosphoric = 1:1.30) pretreated at 421°C for three reaction temperatures. A statistical analysis of the four experiments at 421°C indicated an estimated error of ±4 and ±10% for the rate constants and adsorption equilibrium constants, respectively.

The values of k, the rate constants, K, the adsorption equilibrium constant, the activation energy (as obtained from the values of k), and the apparent heat of adsorption (as obtained from the values of K) are shown in Tables 3–5 for three catalysts and three pretreatment temperatures. Figure 2 displays a typical Arrhenius plot for BPR-1 pretreated at 311°C. The values for the heat of adsorption of 1-propanol were obtained on the assumption that the heat of adsorption, ΔH, is constant over the temperature range in question. Errors in activation energy and heat of adsorption are estimated to be ±2 kcal $mole^{-1}$. The heat of liquefaction at the normal boiling point of 1-propanol is −9.852 kcal $mole^{-1}$ (10). As can be seen from Tables 3–5, in all cases but two, the values of ΔH for adsorption are considerably greater than those for the heat of liquefaction.

Complementary experiments were performed to examine a number of additional variables. For one of the catalyst com-

TABLE 3

Kinetic Constants for *n*-Propanol Dehydration on Catalysts Pretreated at 311°C

Catalyst / Reaction temperature (°C)	BPR-1 (boric:phosphoric = 1:1.30)		BPR-2 (boric:phosphoric = 1:1.11)		BPR-4 (boric:phosphoric = 1:1.51)	
	$k \times 10^2$[a]	K[b]	$k \times 10^2$[a]	K[b]	$k \times 10^2$[a]	K[b]
170	2.66	0.373	2.59	0.697		
175	3.03	0.339	2.80	0.532	2.11	0.343
180	3.82	0.261				
185	4.65	0.250	5.44	0.296	3.20	0.286
190			7.43	0.312		
Activation energy (kcal/mole)	15.4		22.5		17.2	
Apparent heat of adsorption (kcal/mole)	−11.8		−17.9		−7.5	
Surface acidic concentration (mequiv/m^2)	0.031		0.041		0.024	

[a] Units of k, milliliters (STP) per minute per square meter.
[b] Units of K, Torr^{-1}.

TABLE 4

Kinetic Constants for *n*-Propanol Dehydration on Catalysts Pretreated at 421°C

Catalyst / Reaction temperature (°C)	BPR-1 (boric:phosphoric = 1:1.30)		BPR-2 (boric:phosphoric = 1:1.11)	
	$k \times 10^2$[a]	K[b]	$k \times 10^2$[a]	K[b]
170	1.23	0.385	1.29	1.00
175	1.69	0.315	1.71	0.347
185	2.25	0.274	2.94	0.282
195	3.18	0.261	4.91	0.147
Activation energy (kcal/mole)	14.9		21.9	
Apparent heat of adsorption (kcal/mole)	−6.0		−18.0	
Surface acidic concentration (mequiv/m^2)	0.028		0.030	

[a] Units of k, milliliter (STP) per minute per square meter,
[b] Units of K, Torr^{-1}.

TABLE 5

Kinetic Constants for n-Propanol Dehydration on Catalysts Pretreated at 536°C

Catalyst Reaction temperature (°C)	BPR-1 (boric:phosphoric = 1:1.30)		BPR-2 (boric:phosphoric = 1:1.11)	
	$k \times 10^{2\,a}$	K^b	$k \times 10^{2\,a}$	K^b
175	1.11	0.564	0.767	0.633
185	1.66	0.337	2.09	0.302
195	3.47	0.192	4.32	0.173
200	3.96	0.225		
205			6.06	0.101
Activation energy (kcal/mole)	22.7		29.6	
Apparent heat of adsorption (kcal/mole)	−17.3		−25.8	
Surface acidic concentration (mequiv/m^2)	0.015		0.018	

[a] Units of k, milliliter (STP) per minute per square meter.

[b] Units of K, Torr^{-1}.

positions, experiments up to 275°C showed that the conversion continued to increase to approximately 80%. Several experiments in which water vapor was introduced to the propanol–helium stream showed that, in relatively large amounts, water acted to poison the reaction. On the assumption of a Langmuir–Hinshelwood mechanism for the poisoned reactions, a value of the adsorption equilibrium constant for water of 0.12 ± 0.02 was obtained. This demonstrated, under the conditions of reactions where additional amounts of water had not been artificially introduced, that the KP term for water would be negligible compared to that for propanol. This is not to say, however, that it is believed that the effect of water is not important in the present catalytic systems. Indeed, as an example, although relatively large amounts of water may be needed to poison the reaction, there is evidence (*2*) that relatively small quantities of water may replenish active acidic sites on the surface of the catalyst, possibly through dissociation into chemisorbed hydroxyl groups.

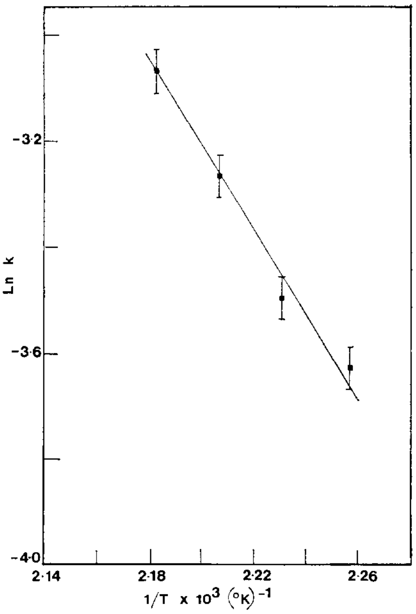

FIG. 2. Arrhenius plot for BPR-1 (boric:phosphoric = 1:1.30) pretreated at 311°C.

At all temperatures of the present experiments, the formation of di-n-propyl ether

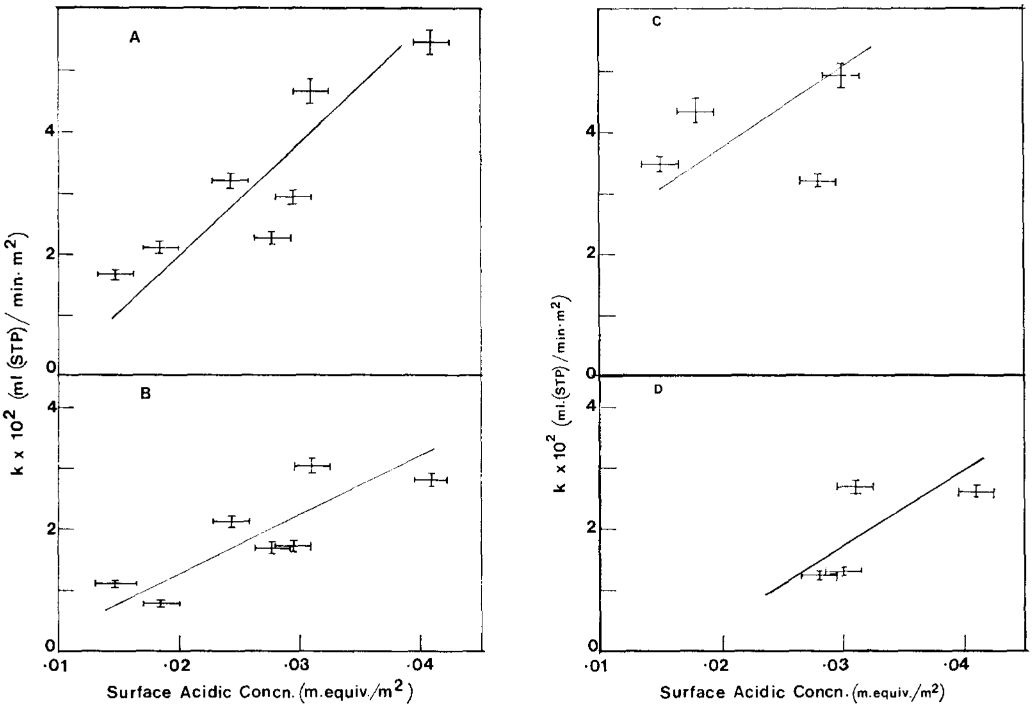

FIG. 3. Effect of surface acidic concentration on the surface reaction rate constant (k). Reaction temperatures are: (A), 185°C; (B), 175°C; (C), 195°C; and (D), 170°C.

is thermodynamically unfavorable while the decomposition of the ether to olefin and water is quite favorable. An experiment was performed in which a mixture of the ether and helium was contacted with the catalyst at 180°C for 40 hr. The products were propylene and water. However, after 10 hr, only approximately 20% decomposition of the ether had occurred, thus suggesting that it was unlikely that the ether is a significant dehydration product of 1-propanol.

A number of correlations can be drawn with the available data. The surface reaction rate constant and absolute value of the heat of adsorption of 1-propanol decrease with increasing *ortho*-phosphoric acid content of the catalyst. The surface reaction rate constant decreases while the activation energy and absolute value of the heat of adsorption increase with pretreatment temperature. The activation energy for a pretreatment temperature of 400°C is somewhat less than that for 300°C but is substantially higher at 500°C. However, the activation energy is slightly lower for a sample of H_3PO_4/H_3BO_3 ratio equal to 1.3 than for one of 1.5 and highest for that of 1.1.

Estimations of total acidic concentrations were obtained through the use of titrations with solutions of n-butylamine in benzene and neutral red as indicator. Figure 3 illustrates that the rate constant increases with the total surface acidic concentration (although the quantity and scatter of the data in Figs. 3C and D make this conclusion somewhat more tenuous in these two cases). This suggests that the catalytic activity depends on the number of acidic sites, either total, or over some more narrow range of acidic strength. Further, the concentrations of acidic sites decreases with increasing pretreatment temperature. Since it would seem (*2*) that this process would be more likely to remove acid centers of the

Brønsted than those of the Lewis type, it is assumed that the acidic sites are predominantly of the former type and that these are the active centers for dehydration. A carbonium ion mechanism in which the alcohol molecule adsorbs on the acidic hydrogen, forms water and a carbonium ion, which itself releases a proton to form the alkene, the released proton regenerating a Brønsted site, and the entire catalytic process occurring on the surface would be consistent with the available data.

The possibility of sizable surface concentrations of Lewis sites cannot be eliminated, however. Work (*11*, *12*) published on alcohol dehydration over catalysts similar to boron phosphate has indicated that the formation of a stable surface alkoxide species is necessary for the production of an ether. This alkoxide species presumably forms on a Lewis acid site. Although little or no ether is formed during the decomposition of *n*-propanol over boron phosphate, sizable quantities are produced during the decomposition of ethanol (*1*). This could indicate that, if ether is produced over boron phosphate via an alkoxide mechanism, Lewis sites are probably present and the absence of ether in the propanol case could perhaps be explained by the lower stability of the larger surface alkoxide species.

Tada and Mizushima (*13*), investigating the dehydration of *n*-butanol over boron phosphate catalysts, observed a similar relationship between catalytic activity and total surface acidic concentration as found in the present work, and Dzis'ko *et al.* (*14*) found such a correspondence for dehydration of ethanol over silica–zirconia catalysts of various compositions. Kibbey and Hall (*12*) found lower rate constants and a higher activation energy (40.1 kcal mole^{-1}) for the dehydration of 1-propanol over hydroxyapatite in the range from 230 to 392°C. Apparent heats of adsorption and activation energies for 1-propanol decomposition to propylene on silica–alumina (*15*) (-4.0 and 16.2 kcal mole^{-1}, respectively) and on molecular sieve 13X (*16*) (-17.0 and 22.6 kcal mole^{-1}, respectively) at temperatures of 232–343°C and 240–270°C for silica–alumina and molecular sieve, respectively, fall within a range similar to those found for boron phosphate. With γ-alumina catalyst, however, Knözinger *et al.* (*17*) found that 1-propanol is decomposed to di-*n*-propyl ether and water exclusively in a temperature range (130–200°C), similar to that employed in the present work.

While alumina and silica–alumina catalysts have been observed to decompose primary alcohols to both olefin and ether, the acidic hydroxyapatite catalysts catalyze only the formation of olefin. Kibbey and Hall (*11*) account for the lack of ether formation on hydroxyapatite, which they claim is characterized by strong Brønsted acidity, by the formation of only widely scattered surface alkoxide species. The alumina surface is known to possess strong Lewis acid sites (*18*) but is thought to exhibit negligible Brønsted activity. Silica–alumina is thought to possess acidic sites of both types.

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