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The Liquid-Phase Dehydration of *tert.*-Butyl Alcohol on B–P–O Catalysts

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The dehydration of *tert.*-butyl alcohol in the liquid phase has been investigated on B–P–O catalysts with phosphorus/boron molar ratios from 0.8 to 1.4 and pretreatment temperatures up to 400°C. A maximum in the initial reaction rate occurs at a P/B of 1.25 and a pretreatment temperature of 100°C. The reaction is catalyzed by Brønsted acid sites and not Lewis acid centers and appears to proceed through a carbonium ion mechanism.

INTRODUCTION

Methods for the characterization of solid catalysts can arbitrarily be divided into two classes, those which use electromagnetic radiation as the probe and those which employ atoms or molecules to examine the surface. There are, of course, techniques, such as the infrared spectroscopic study of chemisorbed species, which can be considered as involving both molecules and electromagnetic radiation. While the two classes of characterization provide complementary information on the surface properties of the solid, the technique in which molecules are employed as probes is, in principle, capable of producing more direct information on the catalytic properties of the solid. It is usually most convenient to employ one-component reactant systems for such experiments and these are normally operated at sufficiently high temperatures so that the reactants are in the gas phase. In order to guarantee adequate contact between gaseous species and solid catalyst and to minimize or effectively eliminate diffusional problems, the experiments often involve a moving gas phase and a stationary catalyst bed.

For measurements of the relative activities of a series of catalysts it would be advantageous to operate with as simple a reaction system as possible. For such purposes a stirred batch reactor with a one-component liquid-phase reactant system is in principle the most convenient. With acidic catalysts a reactant capable of producing tertiary carbonium ions at temperatures less than or equal to the boiling point of the reactant and a product which is gaseous at room temperature and atmospheric pressure is most appropriate. Tertiary butyl alcohol (TBA) fulfills such requirements and has previously been employed by various investigators with a variety of solid catalysts. TBA is a convenient compound for study since tertiary carbonium ions are the most stable and should readily form even in systems held at temperatures at or below the boiling point of the alcohol. Since the energy required to isomerize the tertiary ion to the corresponding secondary or primary species is substantial, the ion tends to remain in its tertiary form, at least at temperatures near the boiling point of TBA, and the process and products are thus of a relatively simple nature.

Frilette *et al.* (*1*) have studied the dehydration of TBA on Dowex 50W. Their results have been further analyzed by Yamanis *et al.* (*2*), and by Frilette (*3*). The

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catalysis of this reaction by various sulfonic acid resins (*4–6*) and more recently by expanding layer silicates (*7*) has also been studied.

Tertiary butyl alcohol and its dehydration reaction are of interest for subsidiary reasons. TBA has been evaluated for antiknock formulations (*8*), gasoline additives (*9*), and gasoline extenders (*10*) and catalyzed dehydration reactions for hydrocarbon fuel manufactures (*11*).

Phosphate catalysts have been reviewed previously (*12*). The present work is concerned with the liquid-phase decomposition of TBA on both stoichiometric and nonstoichiometric boron phosphate catalysts, and the effect of the phosphorus/boron molar ratios (P/B) and pretreatment temperatures on its catalytic activity as evaluated from the dehydration of TBA.

EXPERIMENTAL

Materials. The catalysts were prepared with molar phosphorus-to-boron ratios (P/B) of 0.8, 1.0, 1.2, 1.25, 1.3, and 1.4 from boric acid (Fisher certified ACS grade) and orthophosphoric acid (Fisher). Appropriate amounts of the acids were stirred continuously in a glass reaction vessel at 60°C for 6 h after which the resulting paste was dried in air for 24 h at 150°C. The dried solid was ground and sieved and the 100 to 200-mesh portion was heated at 10^{-3} Torr for 16 h at temperatures ranging from 85 to 400°C. In subsequent discussion 0°C pretreatment refers to a catalyst which had not been pretreated.

Reactions. The catalytic dehydration of TBA was carried out in a liquid-phase stirred batch reactor consisting of a sealed glass vessel vented through a water-cooled condenser to a soap bubble flowmeter. Preliminary experiments were employed to select the most suitable quantities of alcohol and catalyst, stirring rate, and reaction temperature. All results reported here employed 150 ml of TBA and 4.5 g of catalyst at a reaction temperature of 82.5 (±0.5)°C, the latter obtained in a regulated oil bath. The TBA was allowed to equilibrate at this temperature prior to addition of the catalysts. A stirring rate of approximately 350 rpm was attained with a shaped Teflon blade to ensure efficient mixing. A Carbowax 20 M (TPA)/Chromosorb W (60–80 mesh) column was employed to verify the composition of the products from the dehydration.

RESULTS

The cumulative volume of isobutylene produced increases linearly with time for periods up to approximately 1 h, depending on the catalyst composition and pretreatment temperature. Such results are illustrated in Fig. 1 for the catalyst with P/B equal to 1.2. Subsequently, the cumulative volume falls below the extrapolation of the initial straight line, indicating a decrease in the rate of production of isobutylene. The slope of the linear portion of such data is taken as the initial rate of reaction for subsequent discussion.

The initial rate of reaction for the catalysts with P/B equal to 0.8 is relatively low for all pretreatment temperatures (Fig. 2). Catalysts with P/B equal to 1.0 have somewhat higher initial rates, but as can be seen from Fig. 2 the largest increase occurs between P/B of 1.0 and 1.2. A maximum in the rate occurs at a P/B of approximately 1.25, while the rates of those catalysts with P/B of 1.3 and 1.4 are again lower.

The effect of pretreatment temperature is seen most clearly from Fig. 3. The catalysts with P/B of 0.8 show little or no change in reaction rate as the pretreatment temperature is increased up to 400°C. Catalysts with P/B equal to 1.0 have a slightly increased activity when pretreated at 100°C, but display a decrease in activity as the pretreatment temperature is increased. In each case the initial rate increases as the pretreatment temperature is increased and reaches a maximum at a pretreatment temperature of approximately 100°C. With these compositions the initial rate increases by a factor of 2–3 up to a pretreatment tem-

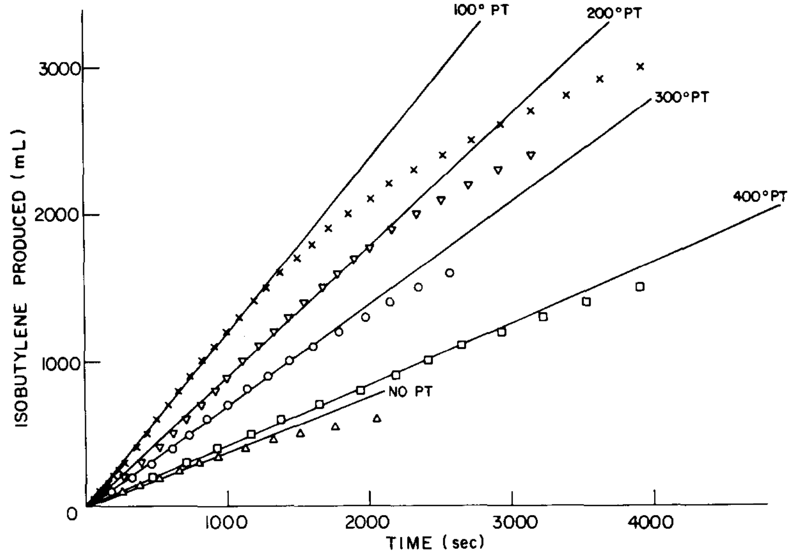

FIG. 1. Cumulative volumes of isobutylene produced as a function of time from *tert.*-butyl alcohol on B–P–O catalysts with P/B = 1.20. △, No pretreatment; ×, pretreatment at 100°C; ▽, at 200°C; ○, at 300°C; □, at 400°C.

perature of 100°C. The activity decreases with further increase in the pretreatment temperature above 100°C. However, pretreatment temperatures between 300 and 400°C, depending on the catalyst composition, are required in order to reduce the initial reaction rate to that observed with the catalysts which have not been pretreated.

The quantity of ammonia chemisorbed per area of the catalyst shows a dependence on pretreatment temperatures (Fig. 4) which is somewhat similar to that shown by the initial reaction rate (Fig. 3). The quantity of NH_3 chemisorbed increases with pretreatment temperature to a maximum at 100°C on the catalysts with P/B equal to 1.2, 1.25, and 1.3 and decreases with further increase in pretreatment temperature. With the 1.4 catalysts, however, the maximum occurs at 200°C. Negligible quantities

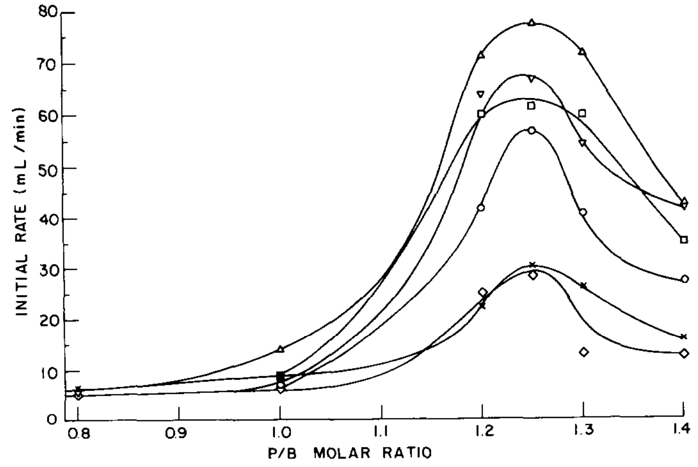

FIG. 2. Initial rates of isobutylene production for various P/B. ×, No pretreatment; □, pretreatment at 85°C; △, at 100°C; ▽, at 200°C; ○, at 300°C; ◇, at 400°C.

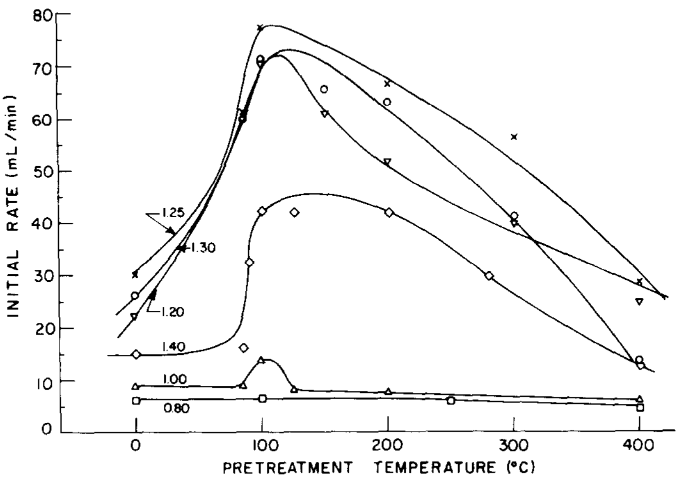

FIG. 3. Initial rates of isobutylene production for various pretreatment temperatures; P/B: □, 0.80; △, 1.00; ▽, 1.20; ×, 1.25; ○, 1.30; ◇, 1.40.

of NH_3 were chemisorbed on the catalyst where P/B is equal to 0.8. The correlation between initial reaction rate per unit area of catalyst and the quantity of ammonia chemisorbed is more readily seen in Fig. 5. The reaction rate increases monotonically with the amount of ammonia chemisorbed for each of the catalysts where P/B is greater than 0.8. The catalyst with P/B equal to 1.2 shows the most steeply rising curve, as expected in view of the data illustrated in Figs. 2–4.

X-Ray band profiles obtained for the various catalyst samples showed similar peaks for all catalyst samples. The most prominent band appeared at a 2θ value of 24.5°.

Additional reaction rate measurements were done with *tert.*-butyl alcohol diluted with various amounts of dried benzene. The initial rate of reaction was found to increase linearly with the concentration of the alcohol, thus showing the reaction at least initially to be first order in the concentration of the alcohol. In addition, the time

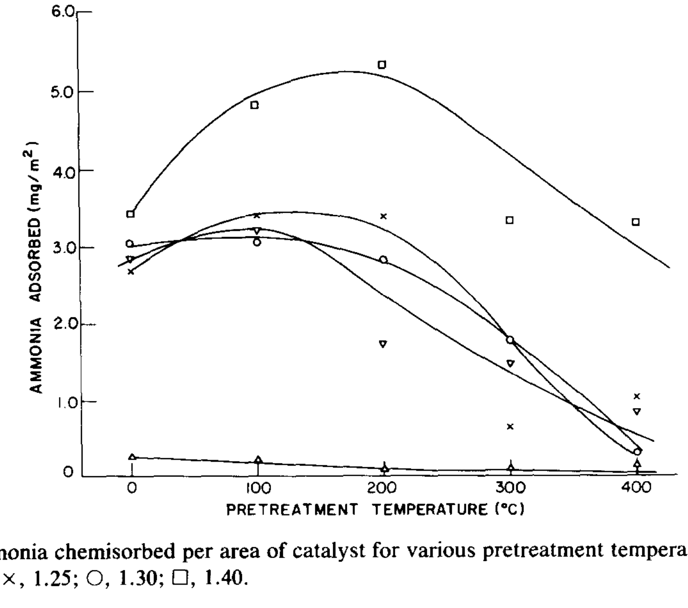

FIG. 4. Ammonia chemisorbed per area of catalyst for various pretreatment temperatures; P/B: △, 1.00; ▽, 1.20; ×, 1.25; ○, 1.30; □, 1.40.

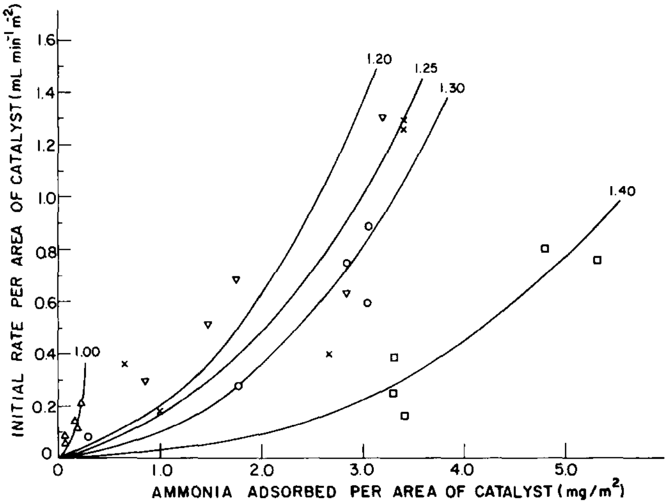

FIG. 5. Initial rate of isobutylene production per area of catalyst versus ammonia chemisorbed per area of catalyst; P/B: △, 1.00; ▽, 1.20; ×, 1.25; ○, 1.30; □, 1.40.

period over which the cumulative volume of isobutylene remained linear with time increased with decreasing concentration of the alcohol. This provides evidence for the probable poisoning effect of one of the products, presumably water.

A number of experiments were done in which measured amounts of water were added to the alcohol prior to the beginning of the reaction and addition of catalyst. In all cases the initial rate of reaction was reduced and the departure from linearity occurred earlier in the process. The initial rate was found to decrease as the amount of water added to the catalyst increased.

DISCUSSION

The production of isobutylene from TBA in the liquid phase is catalyzed by B–P–O catalyst with P/B $\geq$ 1.0, and even those with P/B equal to 1.0 have a relatively small activity. It has previously been shown from infrared spectroscopic studies of chemisorbed ammonia and various pyridines that B–P–O catalysts with P/B $\geq$ 1.0 have predominantly Brønsted acidic sites while those where P/B $\leq$ 1.0 are largely Lewis acidic in nature (*13*, *14*). Consequently, it must be concluded that the presence of Brønsted acidic sites is necessary, but possibly not sufficient, for catalysis of the dehydration of TBA. Since the reaction is acid catalyzed and first order in the concentration of alcohol, a carbonium ion mechanism is highly probable (*15*). It should be noted here that, although the dehydration of TBA diluted with dried benzene could be shown to be first order in TBA, in agreement with the results of other workers (*4*–*6*) on various catalysts, the rate of dehydration of pure TBA, as illustrated in Fig. 1, is zero order, presumably as a consequence of the essentially negligible change in concentration of TBA which occurs in the pure reactant.

In earlier work (*16a*) it was shown that both ethylene and diethyl ether are formed from the gas-phase dehydration of ethanol on a B–P–O catalyst where P/B is equal to 1.12. *n*-Propanol in the gas phase produced only propylene and water on B–P–O catalysts with P/B between 1.0 and 1.5 (*16b*). The rate constants decreased with pretreatment temperature in the range from 300 to 500°C, the maximum in rate appeared at a P/B of approximately 1.3, and the rate constants were shown to correlate with the surface acidic concentration as measured by butylamine titration using neutral red as the indicator. In addition, studies of the oxidation of iodide anion to iodine in nonaqueous solvent at temperatures between 20 and 50°C showed that the amount of iodine produced decreased with increasing pretreatment temperature except for the catalyst with P/B equal to 1.0 where the production was small and constant for all pretreatment temperatures (*17*). The production of iodine increased with P/B for pretreatment temperatures below approximately 200°C, whereas above this temperature a maximum was attained for a catalyst with P/B equal to 1.29.

Flockhart *et al.*, from their work on the oxidation of the iodide anion on zeolites and silica–alumina, concluded that the active sites in the oxidation were of Brønsted rather than Lewis type (*18*). The results of studies on the same reaction with B–P–O catalysts would appear to support such a conclusion and further correspondences with the results of the present work are evident.

The dehydration of gaseous ethanol on B–P–O catalysts has recently been further investigated by Haber and Szybalska (*19*). They have found a maximum in the yield of ethylene at a P/B value of 1.25 and a very small production of ethylene for P/B less than or equal to 0.8 and attribute this behavior to the dominant influence of Brønsted sites at P/B greater than 0.8. The observations of these authors are again consistent with the present results.

In the present work it is found that the catalysts of all compositions, except P/B equal to 0.8, must be pretreated to 100°C under vacuum in order to maximize their activity. Heating to higher temperatures reduces the activity. Temperature-programmed desorption (TPD) studies (*20*) have demonstrated that water is evolved from B–P–O catalysts at four temperatures, approximately 100, 125, 200, and 250°C. The energies associated with the first two peaks are approximately 6 and 14 kcal/mole, which implies that the water evolved was hydrogen-bonded to the surface. The amplitudes of these peaks at 100 and 125°C decrease as P/B increases. The water evolved at 200 and 250°C has desorption energies of approximately 29 and 56 kcal/mole. Since this water is more strongly held to the surface it is probable that it exists on the surface in dissociated form. This is consistent with observations of the infrared spectra of B–P–O after heating to various temperatures and after exposure to water (*21*). For P/B greater than 1.10, the amounts of the water desorbed at 200 and 250°C in the TPD experiments increase as P/B increases.

In the present experiment, pretreatment at 100°C apparently removes the weakly bound water which was presumably held in molecular form, probably hydrogen bonded, on the surface of the catalyst. Although this adsorbed water is expected to act primarily as a steric block to reactant molecules, perturbations in electronic densities of the acidic sites undoubtedly occur.

On increase of the pretreatment temperatures above 100°C the activity of the catalyst begins to decrease. From both the TPD and infrared spectra it is apparent that this must be associated with the loss of more tightly bound water presumably existing as hydroxyl groups and some of which will serve as Brønsted acidic sites.

The water molecules bound to the surface also reduce the amount of ammonia chemisorbed, as would be expected. However, the quantity of ammonia chemisorbed, for all catalysts except that with P/B equal to 1.4, changes relatively little up to a pretreatment temperature of 100°C, while the reaction rate increases by a factor of 2 to 4 in the same temperature range. In addition, the most substantial decreases in the ammonia chemisorption occur at temperatures above 200°C, where the reduction in number of Brønsted sites is appreciable, as evidenced from the loss of more strongly bound water. As has been noted, both the TPD data and infrared spectra suggest that such strongly held water exists in dissociated form on the surface of these catalysts. Thus the chemisorption of ammonia reflects, as a function of the pretreatment temperature, characteristics similar to those of the dehydration reaction, and demonstrates the dependence of reaction rate on the acidity of the catalyst.

The most active catalyst is that with P/B equal to 1.25. Although this catalyst does not possess the largest number of acidic sites, it apparently possesses the highest concentration of those in a suitable range of acidic strengths. The catalyst with P/B equal to 1.4 has a larger number of acidic sites, but apparently a smaller number of these are appropriate for catalyzing the dehydration reaction. The initial-rate data can be approximately related to the amount of ammonia chemisorbed by an equation of the form

$$\left(\frac{\text{Rate}}{\text{Area}}\right) = k\left(\frac{\text{NH}_3}{\text{Area}}\right)^m. \qquad (1)$$

Since it has been shown earlier (*13, 14*) that B–P–O catalysts with P/B greater than one possess acidic sites which are largely Brønsted in nature, while those where P/B is less than one are primarily of Lewis type, the calculated values of m (Table 1) presumably reflect the effectiveness of the particular sites on which ammonia is chemisorbed in catalyzing the dehydration reaction. Since the relative amounts of Lewis and Brønsted sites have been shown to be a function of P/B, such effectiveness should be considered as including both the type and strength of the acidic site.

It appears that the decrease in the rate of reaction at various times, depending on P/B and the pretreatment temperature, results from the deactivation by the water produced in the reaction. The reduction in rate on addition of water prior to the reaction provides evidence for such poisoning by a product of the reaction. It is probable that the water either produced in the reaction or added initially effectively negates the advantageous effect of the pretreatment of the catalyst at elevated temperatures.

TABLE 1

Calculated Values of m from Eq. (1)

P/B	m
1.0	0.33
1.2	0.96
1.25	2.5
1.3	2.1
1.4	0.39

It is of interest to compare observations from the present work with those obtained for the dehydration of TBA on other catalysts. Davidtz (*7*) reported values for the dehydration rates on expanding layer silicates up to 0.3 ml sec^{-1} m^{-2}, which are approximately a factor of 10 larger than the largest values found in the present work. The liquid-phase dehydration of TBA has also been studied on nonporous SiO_2 covered with various quantities of Al^{3+} by adsorption from etheric $AlCl_3$ solutions and calcined at 420–1000°C (*22*). These workers found that the catalytic activity passes through a maximum after heating to 600–700°C. In addition, the activity is essentially zero with pure SiO_2 but increases as Al^{3+} is added. Although both Lewis and Brønsted sites are present on these catalysts, the authors conclude that the activity in the dehydration of TBA is related to the existence of Brønsted sites. Although the evidence from the present work supports the contention that the dehydration of TBA is catalyzed by Brønsted rather than Lewis sites, it is of interest to note the results from a recent study of the adsorption of TBA from the vapor phase on silica (*23*). In that work evidence was found for the existence of aprotonic sites to which TBA could be bound, and further, such structures can be considered as possible intermediates in the dehydration reaction at higher temperatures. However, in spite of such results for silica there is no evidence in the present work for an appreciable activity with B–P–O catalysts of P/B less than 1.0, where Lewis sites would be expected to be in plentiful supply.

ACKNOWLEDGMENT

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