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The Isomerization of 1-Butene on Stoichiometric and Nonstoichiometric Boron Phosphate: The Dependence of the Acidity on Stoichiometry

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The isomerization of 1-butene to cis- and trans-2-butene and isobutene has been studied on boron phosphate (BP) catalysts with P/B ratios from 0.8 to 1.4 and at various reaction temperatures and contact times. Isobutene forms on BP with P/B ratios of 1.2 or higher on which relatively strong Brönsted acid sites exist and increases with reaction temperature up to 400°C. Although deactivation of the catalyst occurs, the activity and selectivity to isobutene can be maintained by the continuous injection of small quantities of water into the feed stream. The conversion and selectivities are related to the formation of carbocations on Brönsted acid sites on the high P/B compositions.

INTRODUCTION

This isomerization of 1-butene is of both fundamental and practical interest (1–12). Isobutene, formed from the skeletal isomerization of 1-butene, is employed as the precursor of methyl tertiary butyl ether and its formation is characteristic of the presence of relatively strong acid sites on heterogeneous catalysts. Recently (1) bimolecular mechanisms have ben proposed as operative in the skeletal isomerization of 1-butene and most recently additional experiments have provided evidence to support the contention that the by-products are formed bimolecularly (8). The 1-butene isomerization process is also of importance in the evaluation of the acidic properties of catalysts and the dependence of these on preparative, pretreatment and reaction conditions (1).

Phosphates have been studied for their catalytic properties for many years (13, 14). The properties of boron phosphate (abbreviated as BP), of particular interest in this laboratory, have been assessed from studies of the conversions of alcohols (15–21), deuterium exchange (22–24), temperature-programmed desorption (25) and infrared spectroscopy (26–28). More recently, the conversion of 2-methylbutanal to isoprene has been studied on stoichiometric and nonstoichiometric BP (29) and the oxidative coupling of methane has been investigated on this as well as a number of other phosphates (30).

The present study reports on the isomerization of 1-butene to the 2-butenes and isobutene on boron phosphate with P/B ratios from 0.8 to 1.4 at various reaction temperatures and contact times and relates the skeletal isomerization to the presence of relatively strong Brönsted acid sites on compositions with P/B greater than unity.

EXPERIMENTAL

Materials

The BP catalysts were prepared from boric (Fisher certified ACS grade) and orthophosphoric (Fisher 85%) acids with preparative P/B ratios of 0.8, 1.0, 1.2, 1.3, 1.4, and 1.6 (denoted as BPX with X equal to the ratio). Appropriate amounts of the acids were stirred continuously at 70°C for 6 h followed by drying in vacuum at 150°C for 24 h. The dried solids were ground and the 100–200 mesh portions were employed for the subsequent experiments.

Measurements

The isomerization of 1-butene was affected in a flow reaction system equipped with a quartz reactor containing 200 mg of sample, except as otherwise indicated. The catalysts were pretreated *in situ* in a flow (20 ml/min) of helium at T_{pt} for 2 h after which the temperature was increased to the reaction temperature (T_{r}) prior to exposure to the feedstream. The reaction system was connected to a gas chromatograph (HP 5890) equipped with a TCD and a 2 m × 1/8 in. OD Carbopack column. No conversion of 1-butene was observed in the absence of catalyst at any of the reaction temperatures employed in the present work. Conversions and selectivities are calculated on a carbon basis:

$$\text{Conversion (\%)} = \frac{\text{Products} \times 100}{\text{Products} + \text{Residual butene}}$$

$$\text{Selectivity to } \iota\ (\%) = \frac{\text{Product } \iota}{\text{Total products}} \times 100.$$

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Temperature-programmed desorption experiments were performed in the reaction system. Effluents were either led directly to the TCD detector or were passed to a GCMS system (HP5890, HPMS5970).

^{1}H MAS NMR spectra were obtained on a Bruker AMX-500 with an external reference of benzene at room temperature. The spinning rate ranged between 6.5 and 8 kHz, depending upon the sample.

RESULTS

The effects of changes in the P/B ratio and of the reaction temperature, the latter for values of 100, 200, 300, and 350°C are summarized in Fig. 1. With the BP 0.8 sample the conversion of butene is less than 5% at all temperatures while up to 350°C no isobutene is observed. The cis/trans ratio of 2-butene for this composition is greater than unity up to 300°C but slightly less at 350°C. In comparison, at equilibrium the cis/trans ratio is less than unity at all temperatures between 300 and 1400 K (Table 1). On increase of the P/B ratio to 1.0 the conversion increases but, as with the 0.8 composition, no isobutene is observed until a temperature of 300°C is reached. The cis/trans ratio for 2-butene remains greater than unity.

TABLE 1

Equilibrium Composition Percentages for 1-Butene and Its Isomers

T(°C)	1-Butene	*Cis*-2-butene	*Trans*-2-butene	Isobutene
100	3	11	26	60
200	6	14	28	52
300	10	16	28	46
350	12	17	28	43

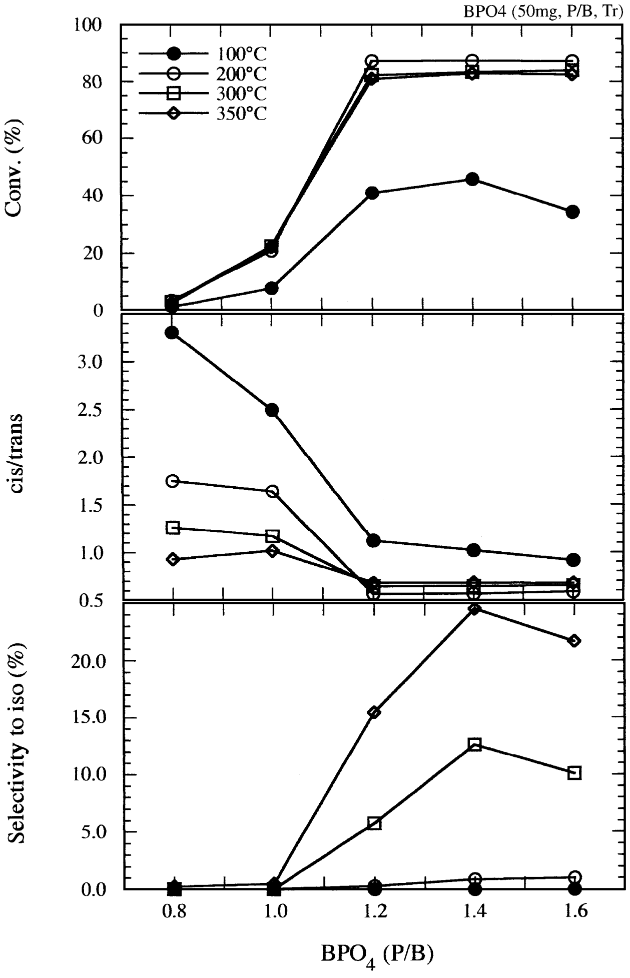

FIG. 1. Effect of the P/B (molar ratio) and reaction temperature on the conversion of butene and selectivities to the products. $W = 50$ mg, $F = 13.7$ ml/min.

The observations with the compositions for which P/B is 1.2 or higher are significantly different from those where P/B is lower. With the former the conversions at the lowest temperature (100°C) are significantly larger, reaching as high as 40%, the cis/trans ratios are approaching unity while selectivities to isobutene remain vanishingly small. With increase in temperature to 200°C and higher the conversions increase markedly to values of 80–90%, the cis/trans ratio decreases to 0.6–0.7 and both are relatively independent of both temperature and composition. Concomitantly the skeletal isomerization product becomes significant at 200°C and reaches 15–25% at 350°C, showing dependence on the catalyst composition at the two highest temperatures.

The temperature at which the catalysts with P/B greater than 1 are pretreated has little or no effect on the conversion and selectivities until 450°C is reached at which pretreatment temperature the conversion and selectivity to isobutene both decrease for a reaction temperature of 400°C (not shown).

In addition to the isomers of 1-butene, small quantities of propylene, *n*-butane, isobutane, pentenes, and octenes were detected in the effluent (Table 2).

With the catalysts of P/B greater than 1 the selectivity to isobutene increases with residence time to ultimately reach a plateau (Fig. 2), indicative of equilibrium with respective to both double bond and skeletal isomerization. Concomitantly, as expected, the selectivities to t2B and c2B decrease with the former remaining slightly larger than the latter.

TABLE 2

Selectivity[a] to Minor Products[b]

Product	350°C	400°C	450°C
C_3	0.9	1.4	2.1
Isobutane	0.4	0.5	0.5
$>C_4$	0.5	0.8	0.4

[a] Percentage.

[b] $P/B = 1.6$, $W = 200$ mg, $F = 13.7$ ml/min.

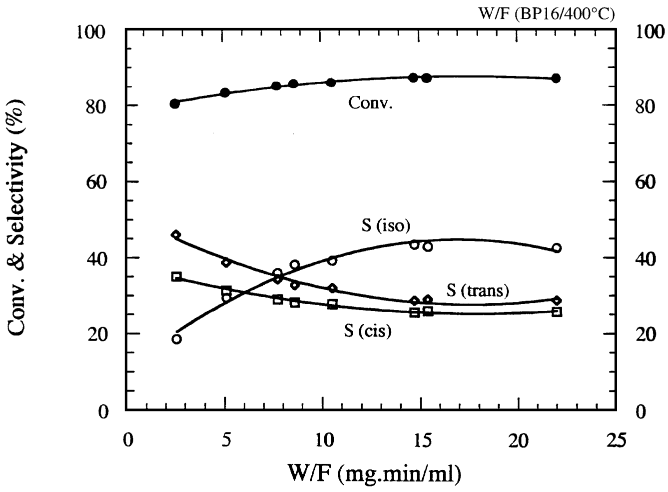

FIG. 2. Conversion of 1-butene and selectivities to products at various residence times. Reaction temperature, 400°C, $W = 200$ mg, $F = 13.7$ ml/min, P/B = 1.6.

With increasing time-on-stream changes in the product composition are observed. As illustrated with PB 1.4 in Fig. 3 both the conversion and the selectivity to isobutene decrease while that to t2B and c2B increase. However, with the continuous addition of small partial pressures of water vapour to the reaction feed stream the aforementioned changes are considerably reduced.

Little or no visual evidence for the formation of carbon was found under the conditions and times on-stream in the present work.

Temperature-programmed desorption (TPD) of the BP samples show the presence of at least two overlapping peaks, both due to the desorption of water (Fig. 4). The lower temperature peak at 150–300°C results from the desorption of water which exists on the catalysts as molecular water, while the higher temperature peak which is seen in the 400–600°C range is due to the associative desorption of water formed from protons and hydroxyl groups on the surface of the solid (25). The latter peak can be seen to increase in intensity as the P/B ratio increases, indicating an increase in the number of protons with P/B ratio. Prior exposure of the samples to NH_3 at 100°C followed by TPD produces peaks resulting from the desorbed NH_3 which begin to emerge at 300°C and whose magnitude increases with P/B ratio (Fig. 5). It is of interest to note that with BP 1.6, for example, sizeable quantities of NH_3 continue to desorb at temperatures as high as 600°C. The quantities of NH_3 desorbed from the various samples are summarized in Table 3.

TABLE 3

Ammonia Desorbed from B-P-O Catalyst[a]

Catalyst	μmol/g
BP08	38
BP10	33
BP12	1293
BP14	2925
BP16	4452

[a] Samples were pretreated in helium flow at 400°C for 2h and 3 × 10 ml of NH_3 was injected upstream at 100°C.

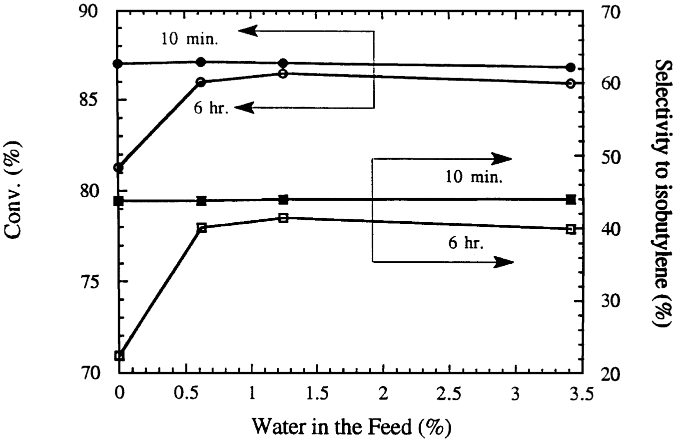

FIG. 3. Changes in conversion and selectivities for various times-on-stream and the effect of the introduction of small quantities of water to the feedstream. Reaction conditions as in Fig. 2 except for the addition of water.

^{1}H MAS NMR spectra of 0.8, 1.0, and 1.4 P/B compositions show a number of peaks, some of which are of relatively insignificant intensities (Fig. 6). With increasing P/B both the chemical shifts and the relative intensities of the two principal peaks increase. Exposure of the 1.4 P/B sample to water vapour produces relatively little change in these peaks. However, after exposure to 1-butene the relative intensities of the peaks from the 1.4 P/B sample decrease although the chemical shifts are relatively unchanged. After the latter sample is exposed to water vapour the intensity of the principal peak has approximately regained its value prior to exposure to 1-butene.

DISCUSSION

BP with P/B ratios less than or equal to 0.8 are evidently not effective in either the conversion of 1-butene or its isomerization to isobutene while those with P/B greater than one produce significant quantities of isobutene. Since infrared spectroscopic studies of pyridine, 2,6-dimethylpyridine, 2,5-dimethylpyridine, and 2,6-ditert-butylpyridine on stoichiometric and nonstoichiometric boron phosphate have shown that BP with P/B ratios greater than unity possesses predominantly Brönsted acid sites while those with P/B less than one are largely Lewis in nature (26), it appears that the isomerization process on BP catalysts is largely occurring on Brönsted acid sites,

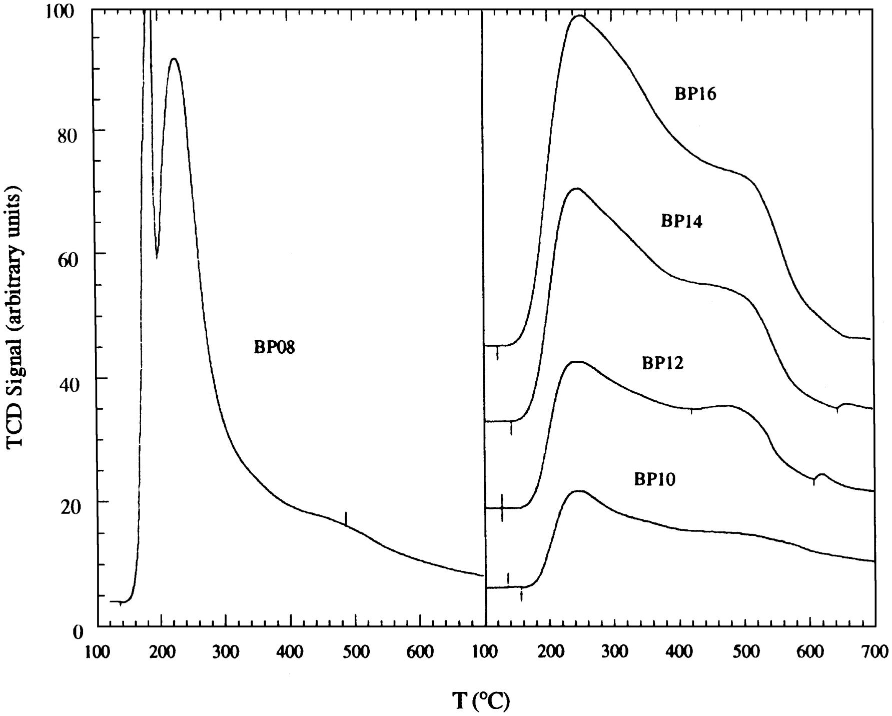

FIG. 4. Temperature-programmed desorption patterns of the BP samples after pretreatment at 110°C for 2 h in a flow of helium.

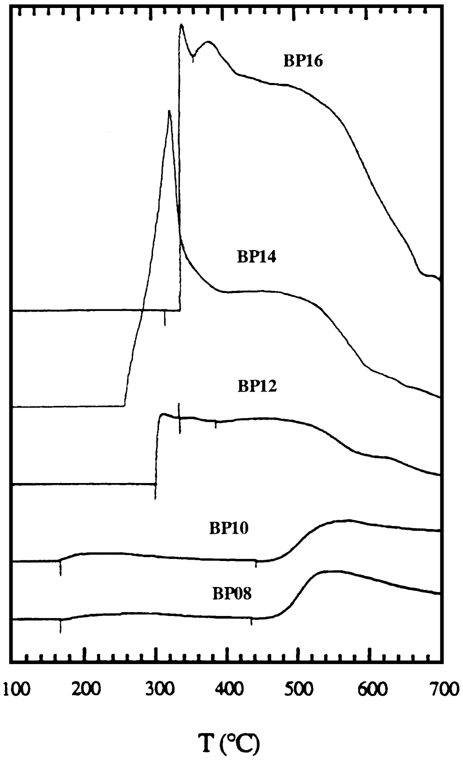

FIG. 5. Temperature-programmed desorption of NH_3 from BP samples. Samples were pretreated in situ in a helium flow at 400°C for 2 h followed by exposure to 30 ml (STP) of NH_3 at 100°C. TPD conditions: carrier gas, helium; heating rate 12°C/min. The signals from BP 0.8 and BP 1.0 were enlarged by a factor of 2.

consistent with the consensus in the literature (1), although Lewis acidic and Lewis acidic–Lewis basic sites have also been mentioned (12). Earlier work (13, 14) has provided evidence for the increase in the number of strong Brönsted acidic sites as the P/B ratio increases above 1. The results of the TPD studies with NH_3 reported in the present work, together with the ^{1}H MAS NMR chemical shifts provide additional support for this contention. The observation of a vanishingly small selectivity to isobutene with the P/B ratio of 1.0 which, however, increases as the P/B ratio increases, at least up to 1.4 while the selectivities to the 2-butenes decrease, is consistent with the requirement of strong Brönsted acid sites for the generation of isobutene in contrast with a relatively facile production of the 2-butenes.

The variance of values of the conversion with P/B ratio (where $P/B > 1$) and reaction temperature (200–350°C) suggests that equilibrium with respect to the double-bond shift process has been achieved at these temperatures and with these catalyst compositions, but not with respect to skeletal isomerization. The observations that the selectivities to the 2-butenes decrease while that to isobutene increases with increasing temperature and increasing contact time suggest that the 2-butenes are precursors to isobutene. The aforementioned may be rationalized by postulating that a secondary carbocation is formed from 1-butene, cis-, and trans-2-butene in the presence of weak acidic sites and an equilibrium established between these four species (Fig. 7). Given the appropriate conditions of sufficiently

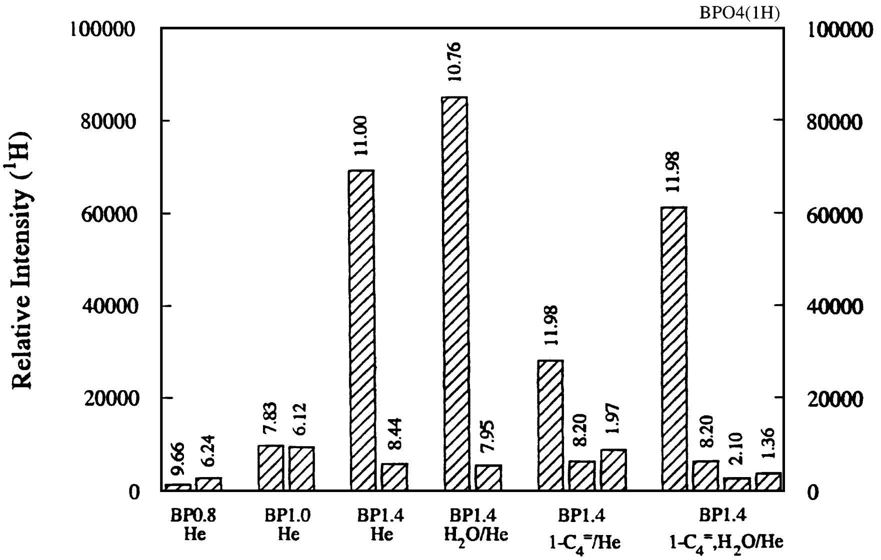

FIG. 6. ^{1}H MAS NMR of BP samples with P/B equal to 0.8, 1.0, and 1.4 pretreated at 400°C for 2 h in indicated environment.

high temperature and strength of acidic sites the secondary carbocation may be converted to the primary analogue which forms the isobutene by loss of a proton. Thus, as the isobutene is formed the 2-butenes will be depleted. It should be recalled that the mechanism usually proposed for the conversion of a secondary to a primary carbocation involves a 1,2-methyl shift to generate a methylcyclopropyl intermediate.

Although polemics concerning the bimolecular mechanism for the skeletal isomerization of 1-butene have

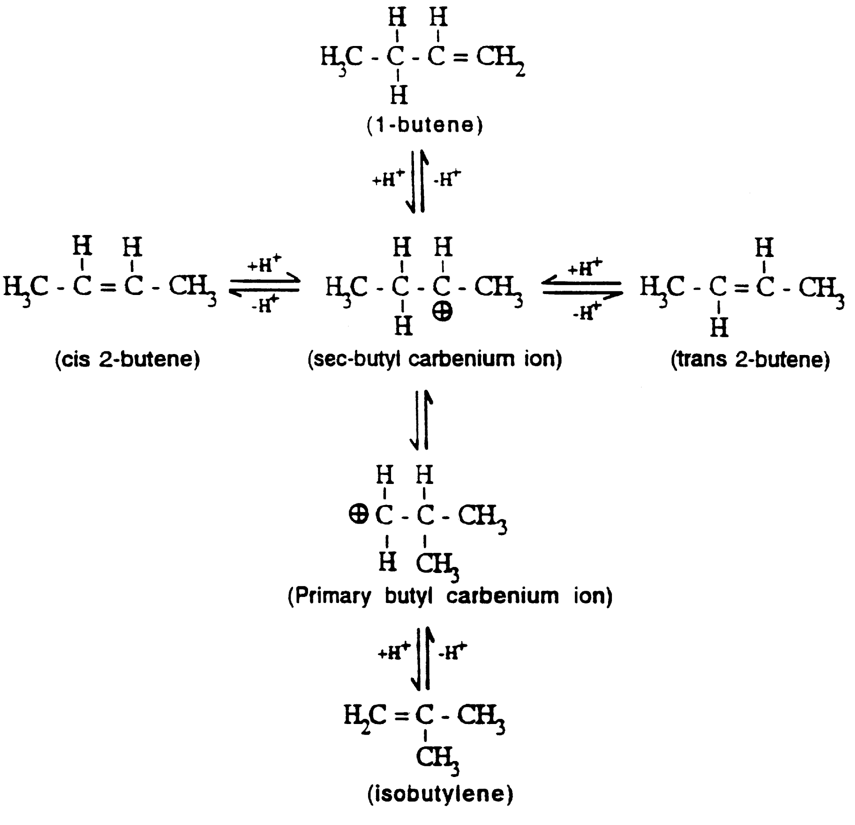

FIG. 7. Carbocation mechanism for isomerization of 1-butene.

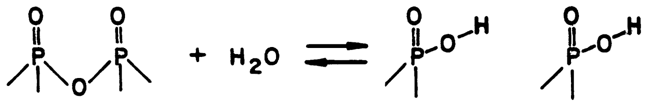

FIG. 8. Dehydration–hydration of BP.

recently appeared (31–33) the evidence in the present work is consistent with a predominantly monomolecular mechanism as advocated by Ponec (1), although the formation of C_3 hydrocarbons, albeit in small quantities, suggests that a bimolecular process may be operative in the production of byproducts.

Earlier temperature programmed desorption studies on BP of various P/B ratios have shown that four peaks, each due to the desorption of water and having activation energies of 6, 14, 29, and 56 kcal/mol are observed at temperatures of approximately 100, 125, 200, and 250°C, respectively (25). The first two peaks have been attributed to the desorption of molecular water, probably hydrogen-bonded to the surface while the latter two result from the associative desorption of water which existed as hydroxyl groups on the surface. The number of surface hydrogen atoms has been estimated as 8×10^{18} atoms/m^2 from the exchange of deuterium from the gas phase and similar numbers were found for the number of empty sites (22). Thus the decrease in activity of the catalysts with P/B greater than 1 after pretreatment at 450°C can be ascribed to loss of surface protons in the form of desorbed water.

The regeneration of the catalyst during the isomerization process by the concurrent onstream addition of small partial pressures of water vapour can be attributed to the dissociative adsorption of water to regenerate the surface hydroxyl groups (Fig. 8). Infrared spectra have shown that water adsorbed on dehydrated BP is partially dissociated to form BOH and POH groups (28).

The ^{1}H MAS NMR spectra contain two peaks for the samples with P/B ratios of 0.8, 1.0, and 1.4. As the P/B ratio increases at least one of the peaks intensifies and the chemical shift increases consistent with the expected increase in the number of protons as well as the acidic strength (34). On exposure of the BP (1.4) sample to water vapour the intensity of one of the ^{1}H peaks increases, indicative of the sorption of water. Exposure of the same sample to 1-butene reduces the intensity of the principal peak while the introduction of water vapour largely restores the intensity, consistent with the aforementioned rationalization of the regenerative effect of introducing water vapour.

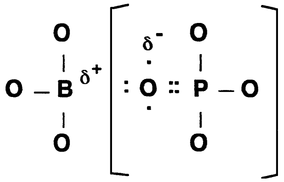

FIG. 9. Structure of BP.

Lastly, a few remarks concerning the structure of stoichiometric and nonstoichiometric BP may be of value. BP has been shown to be isostructural with one or more forms of SiO_2 with both the phosphorus and boron surrounded by a tetrahedron of oxygen atoms (35). Although the P-O and B-O bonds in the network of tetrahedra may be considered as σ-bonds as in SiO_2 the P-O and B-O internuclear separations are 1.55 and 1.44 Å, respectively, and the former corresponds to approximately 1/3 π-bond per σ-bond. The network structure of tetrahedra may thus be represented as one in which the boron atom and the PO_4 group are positively and negatively charged, respectively, superimposed on the aforementioned σ-bonded structure (Fig. 9). Such a representation may explain, at least in part, the increase in Brönsted acidity as the P/B ratio increases.

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