The isomerization of 2-methyl-2-pentene on stoichiometric and nonstoichiometric boron phosphate

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The isomerization of 2-methyl-2-pentene has been studied on boron phosphate (BP) catalysts with P/B ratios from 0.8 to 1.6 and at various reaction temperatures and contact times. Double-bond shift occurs on the compositions with P/B of 1.0 and less, while methyl shifts occur on samples with P/B of 1.2–1.6, demonstrating the presence of strong acidity on the latter solids. Ammonia chemisorption and proton MAS NMR is employed to provide supplementary evidence of the variation in acidity with composition. Although BP of P/B < 1 contains predominantly Lewis acid sites, 2-methyl-2-pentene isomerizes through carbocations, which are formed on the strong Brønsted acid sites on BP with P/B > 1.

Keywords: isomerization, boron phosphate, 2-methyl-2-pentene

1. Introduction

Phosphates are well known as effective catalysts for a variety of processes [1,2]. Although the morphological and catalytic properties of phosphates are dependent on the nature of the cation, aluminum phosphate has undoubtedly received the most attention as a result of its molecular sieve structure. Although less studied, the catalytic properties of the phosphates are also dependent on their stoichiometries, that is the cation/anion ratios.

Boron phosphate (BP) is of interest as a catalyst at least in part as a consequence of its structural similarities to silica–alumina. Tetrahedra with B and P at their centres and oxygen at their vertices form three-dimensional networks similar to that found with silica but with Si replaced by alternating B and P atoms. Nonstoichiometric forms where B/P $\neq 1$ can be produced in which the alternating sequence will be broken.

BP, in stoichiometric and a variety of nonstoichiometric forms, has been characterized by infrared [3–8], electron paramagnetic resonance [9], and diffuse reflectance spectroscopy [10], physisorption of rare gases [11,12], deuterium exchange [13–15], temperature-programmed desorption [16] and scanning electron microscopy [17]. The results of the studies of a number of catalyzed reactions including the conversion of 2-methylbutanal to isoprene and the oxidative coupling of methane as well as techniques for the preparation of BP in mesoporous form have been reported [18–29]. These various studies, in particular those concerned with the infrared spectroscopy of adsorbed pyridine, have shown that the acidity of boron phosphate with P/B ratios greater than one is primarily due to Brønsted sites while that of those with excess boron is Lewis in nature [6]. The results from the various probe reactions have provided supportive evidence for such conclusions.

The present work reports on the results of a study of the isomerization of 2-methyl-2-pentene (2M2PE) on stoichiometric and nonstoichiometric boron phosphate. The isomerization of 2M2PE as a means of evaluating acidity was first proposed by Kramer and McVicker [30].

2. Experimental

2.1. Materials

All methylpentenes and hexenes were purchased from Aldrich with purities of 96% or greater. Dimethylbutenes (99%) were obtained from Chemical Supplies Co.

The BP catalysts were prepared from boric (Fisher certified ACS grade) and orthophosphoric (Fisher 855) 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.

2.2. Measurements

The isomerization of 2-methyl-2-pentene was affected in a flow system equipped with a quartz reactor containing 50 mg of sample. The catalysts were pretreated *in situ* in a flow (20 ml/min) of helium at 350 °C for 1 h after which the temperature was increased to that to be employed in the reaction while the helium flow was maintained. The reaction system was connected to a gas chromatograph (HP 5890) equipped with an FID and a 50 m PONA capillary column.

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Table 1
Surface areas (m^2/g).[a]

Pretreatment temperature	Catalyst composition (mol P/mol B) 0.8	1.0	1.4
200	7.9	4.5	5.4
250	–	–	6.1
300	–	–	5.8
350	–	–	6.6
400	10.0	5.7	14.5

[a] After pretreatment in helium flow at the given temperature for 2 h.

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).

^1H 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.

The surface areas of the catalysts of various stoichiometries were obtained by BET analyses of the nitrogen adsorption isotherms obtained at 78 K with a standard volumetric apparatus outfitted with MKS Baratron capacitance manometers. The BET surface areas are reported in table 1.

3. Results and discussion

The conversion of 2M2PE and the selectivities to the principal products on BP of various P/B (molar) ratios are shown in figure 1 for a reaction temperature of 300 °C. To obtain information on the fresh catalysts the conversions and selectivities shown were obtained after 10 min on-stream in order to reduce or eliminate deactivation and/or coking effects. The conversion of 2M2PE on the excess boron catalyst (P/B = 0.8) is approximately 30%, increases slightly with increase of P/B to 1.0 and reaches a plateau at 75% for catalysts with P/B equal to 1.2–1.6. With the 0.8 catalyst the isomerization product resulting from a (2–1) double-bond shift (2M1PE) dominates, with small selectivities (less than 5%) to 4M2PE and 2,3-dimethyl-2-butene (2,3-DM2BE). As the P/B ratio is increased the selectivity to 2M1PE decreases while those to the (2–3) methyl shift products 3-methyl-2-pentene (3M2PE), 3-methyl-1-pentene (3M1PE), 4M2PE and 2,3-DM2BE increase to reach plateaus for the 1.2–1.6 composition. Small selectivities to hexene are also observed for the 1.2–1.6 compositions, apparently reaching a maximum for BP1.4. Little or no evidence of the formation of molecules larger than C_6 was found under any of the conditions employed in the present work although coking was noted at the higher reaction temperatures and higher times-on-stream than reported here.

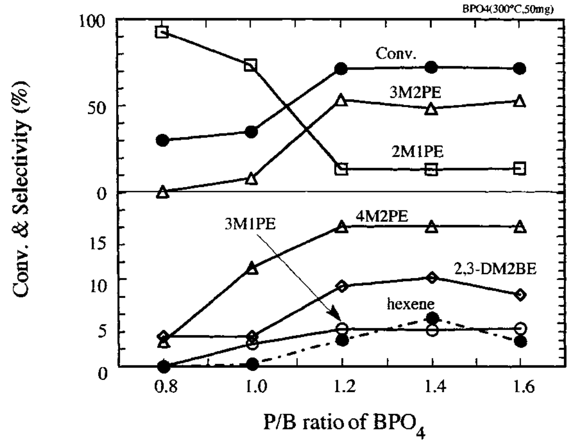

Figure 1. Conversion of 2-methyl-2-pentene and selectivities to the products on boron phosphate of various P/B ratios at 300 °C. $W = 50$ mg, $F = 14$ ml/min, $C_{\text{2M2PE}} \approx 42\%$.

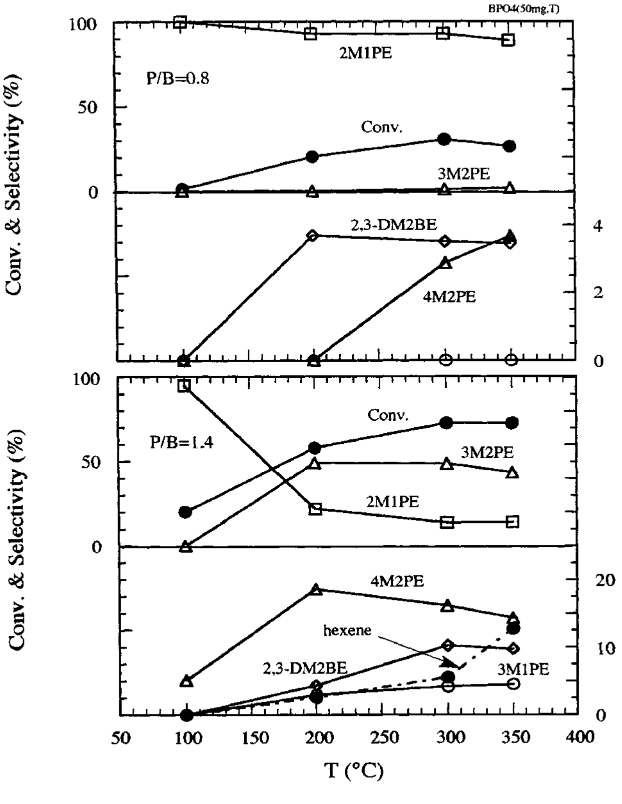

Figure 2. The effects of reaction temperature on the conversion of 2M2PE and selectivities illustrated with boron phosphate of P/B equal to 0.8 and 1.4. $W = 50$ mg, $F = 14$ ml/min, $C_{\text{2M2PE}} \approx 42\%$.

To illustrate the dissimilar effects of temperature on the different stoichiometries BP0.8 and BP1.4 are shown in figure 2. With BP0.8 the selectivity to 2M1PE is 90% or greater at all temperatures from 100 to 350 °C. The selectivity to 2,3-DM2BE becomes significant (4%) at 200 °C while that to 4M2PE reaches 3% at 300 °C. With BP1.4 the selectivity to 2M1PE is greater than 90% at 100 °C but decreases markedly with increase in temperature. Selectivities to the remaining products increase with temperature although those to 3M2PE and 4M2PE decrease somewhat for temperatures higher than 300 °C. With BP1.4 the selectivity to 2M1PE is greater than 90% at 100 °C but decreases markedly with increase in temperature. Selec-

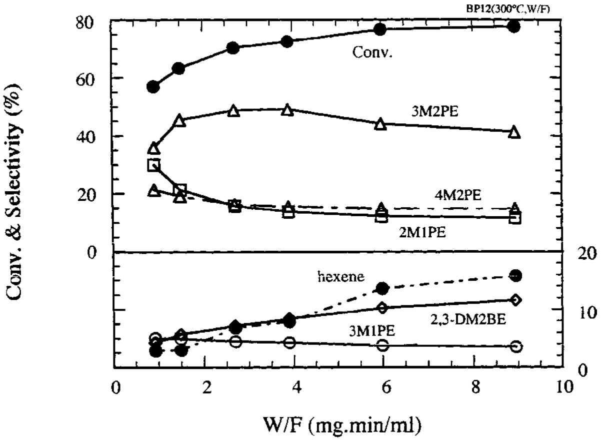

Figure 3. The effect of contact time on 2M2PE reaction illustrated with boron phosphate of P/B equal to 1.2. $T_R = 300\,°C$, $C_{2M2PE} \approx 4.2\%$.

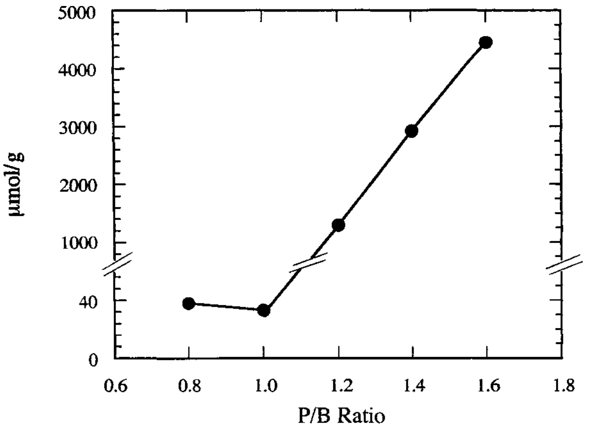

Figure 4. Quantities of NH_3 desorbed from boron phosphate of various P/B ratios.

tivities to the remaining products increase with temperature although those to 3M2PE and 4M2PE decrease somewhat for temperatures higher than 300 and 200 °C, respectively.

The effect of contact time on BP1.2 at 300 °C is shown in figure 3. At low contact time the selectivity to 3M2PE increases while those to 2M1PE and to 4M2PE decrease. 3M2PE appears to form, at least in part, from 2M1PE and 4M2PE, the former resulting from a (2–1) and the latter from a (2–3) double-bond shift.

Temperature-programmed desorption studies show that the quantities of NH_3 desorbed from the 1.2–1.6 compositions are substantially larger than those from the 0.8 and 1.0 catalysts (figure 4), although NH_3 begins to desorb from the former at 250–300 °C and continues to 700 °C or higher while the desorption from the 0.8 and 1.0 compositions begins at 450–500 °C (not shown).

Proton MAS NMR measurements show that the chemical shift is larger for the BP1.4 sample than for the 0.8 and 1.0 compositions and the intensity of the major peak with the 1.4 sample is a factor of five higher than that found with the 1.0 composition (figure 5).

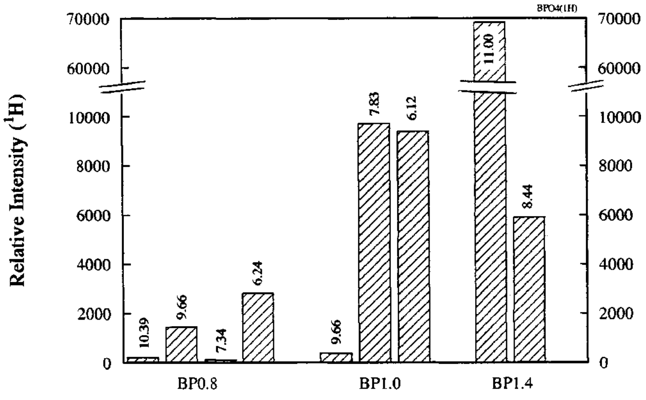

Figure 5. Chemical shifts and intensities from proton MAS NMR measurements on boron phosphate of P/B equal to 0.8, 1.0 and 1.4. Samples are treated at 400 °C in helium flow for 2 h.

4. Discussion

Earlier infrared spectroscopic studies of pyridine, 2,6-dimethylpyridine, and 2,6-di-*tert*-butylpyridine on boron phosphate of various stoichiometries have shown that boron phosphate with P/B greater than one contains primarily Brønsted acid sites, while those with P/B equal to or less than one are largely Lewis in nature (table 2).

Temperature-programmed desorption (TPD) of the BP samples has shown the presence of at least two overlapping peaks, both due to the desorption of water [16]. The lower temperature peak (150–300 °C) has been attributed to the desorption of water which exists on the catalysts as molecular water, while the higher temperature peak (400–600 °C) resulted from the associative desorption of water formed from protons and hydroxyl groups on the surface of the solid. The latter peak increased in intensity as the P/B ratio increased, showing an increase in the number of protons with the P/B ratio. The present NH_3 desorption and proton MAS NMR data are consistent with the earlier TPD data in demonstrating the increase in numbers of protons with P/B.

The increase in conversion of 2-methyl-2-pentene with increase in the P/B ratio can be attributed to the aforementioned increase in the number of protons as well as the nature and strength of the acidic sites as the ratio increases. The invariance of the conversion at 300 °C with P/B ratio from 1.2 to 1.6 is probably indicative of equilibrium at least with respect to the residual quantity of 2M2PE. With BP0.8 the product of a 1,2-hydride shift, that is, a double-bond shift, (2M1PE) dominates and is indicative of weak acidity [30]. It should be empha-

Table 2
Brønsted and Lewis acid site densities.[a]

Sample	Apparent integrated intensity		Acidity (%)	
	A_{1462}	A_{1535}	Lewis site	Brønsted site
BP1.2	249	733	12.1	87.9
BP1.0	873	395	47.3	52.7
BP0.9	606	–	100.0	0.0

[a] Taken from [6].

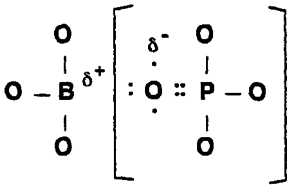

Figure 6. Structure of boron phosphate.

sized that the BP catalysts with P/B $\leqslant 1$ are not devoid of acidity since, as noted above, the earlier spectroscopic data showed the presence of Lewis acidity. Furthermore, the production of isoprene from 2-methylbutanal has been shown to occur preferentially on catalysts with P/B less than 1.0 [26].

The increase in the selectivity to 3M2PE, the product of a (2–3) methyl shift, with increasing P/B demonstrates that catalysts of P/B from 1.2 to 1.6 possess strong Brønsted acidity and the observation of a significant selectivity to 2,3-DM2BE suggests that sites stronger than those required for the formation of 3M2PE are also present.

The present results suggest that the isomerization of 2M2PE on BP occurs via a carbocation mechanism [30] with the latter being formed from the protons attached to the surface oxygen atoms of the phosphate groups. Although the P and B atoms in BP are surrounded by a tetrahedron of oxygen atoms, the relatively short internuclear separations have been attributed to partial π-bonding. Thus, although phosphate anions are not expected to exist as such in boron phosphate, some ionic character will be present, with the PO_4 group negatively charged, which undoubtedly contributes to the increase in Brønsted acidity as the P/B ratio increases (figure 6).

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