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Silica-Supported Boron Phosphate Catalyst Prepared by Chemical Vapor Deposition

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A silica-supported boron phosphate (BPO_4) catalyst was prepared by chemical vapor deposition (CVD) using mixtures of boron triethoxide and phosphoryl trimethoxide. Both the amount and the P/B ratio of deposited BPO_4 were changed with the CVD temperature and time. At the optimum CVD temperature of 300 °C, the amount of deposited BPO_4 was linearly increased with the CVD time. When alkoxide mixtures with the desired P/B ratio were used as CVD sources at 300 °C, the expected P/B ratios were available. At CVD temperatures below 300 °C, neither a sufficient amount nor a desired P/B ratio was given. On the other hand, above 325 °C, the deposition was suppressed by blocking the micropore of silica, especially for long-time CVD operation, owing to the too fast deposition. Although the resulting surface compound was amorphous, it was revealed to have microstructures of BPO_4 by means of a ^{31}P NMR measurement. The amorphous BPO_4 dispersed highly on silica exhibited a high catalytic efficiency for the isomerization of 1-butene and a simultaneous oligomerization of 1-butane in comparison with a catalyst prepared by the conventional impregnation method.

Boron phosphate (BPO_4) is known to be a solid acid which is an effective catalyst for various organic reactions such as hydration,1) dehydration,2–5) alkylation,6–8) and oligomerization.9,10) The catalytic activities depend on the ratio P/B. In a region including excess phosphorus, BPO_4 catalysts have a large percentage of Brønsted acid sites,2,11) and exhibit catalytic activities for such reactions as the hydration of ethylene,1) the dehydration of ethanol to ethylene,2) and the oligomerization of 1-decene.10) In contrast, in a region including excess boron, BPO_4 catalysts consist predominately of Lewis acid sites,2,11) and show catalytic efficiencies for the dehydration of ethanol to diethyl ether,2) the dehydration of 2-methylbutanal to isoprene,5) the ethylation of phenol,8) and the Beckmann rearrangement of cyclohexanone oxime.2) Unsupported BPO_4, however, has a relatively small surface area and its catalytic activity is often poor. Whereas BPO_4 with surface areas of more than 100 $m^2 g^{-1}$ have been reported,12,13) carefulness is required for any reproducible preparation. In addition, it is difficult to impregnate a support material with uniform BPO_4 because of its poor solubility.

Several attempts have been made to prepare a supported type of solid acids such as silica-supported boria,14) alumina-supported boria,15) and alumina-supported silica16,17) by means of chemical vapor deposition (CVD) using the respective metal alkoxides. The alkoxides were easily decomposed into the respective metal oxide on the surface of the support in the presence of oxygen. The highly dispersed boria catalysts, having a weak interaction with the support materials, exhibited an excellent catalytic efficiency for a vapor-phase Beckmann rearrangement of cyclohexanone oxime.14,15) The alumina-supported silica, having a strong interaction between the silica and alumina to form composite-oxides on the surface of alumina support, showed high catalytic activities for several organic reactions such as cracking, isomerization, and dehydration,16,17) which was comparable to those of commercial silica–alumina catalyst.

In the present work, we prepared a silica-supported boron phosphate catalyst (CVD BPO_4/SiO_2) by the simultaneous deposition of boron and phosphorus components onto a silica surface using a mixed vapor of boron triethoxide and phosphoryl trimethoxide, and investigated both the structural and catalytic properties of the deposited boron phosphate.

Experimental

A CVD BPO_4/SiO_2 catalyst was prepared by bringing a mixture of boron triethoxide ($B(OEt)_3$) and phosphoryl trimethoxide ($PO(OMe)_3$) into contact with a silica (ID type gel supplied by Fuji Davison Chemical Ltd.: surface area, 145 $m^2 g^{-1}$; pore volume, 1.0 $cm^3 g^{-1}$; particle size, 0.1—0.6 mm.) in a CVD reactor described previously.17) The mixture of alkoxides with the prescribed P/B ratio, containing 5 wt% methanol, was supplied together with air as a carrier gas (400 $mmol\,h^{-1}$) at a flow rate of 1.7—2.4 mmol h^{-1}. Both the BPO_4 loading and the P/B ratio in the catalyst sample were determined by the alkalimetric titration of H_3BO_3 and H_3PO_4, which were extracted from the sample with hot water. The extracted H_3PO_4 was titrated with sodium hydroxide, followed by titration of the extracted H_3BO_3, whose acidity was strengthened by addition of mannitol. An impregnation catalyst (IMP BPO_4/SiO_2) was obtained by immersing a silica support in an aqueous solution of H_3BO_3 and H_3PO_4, drying at 110 °C and calcining at 300 °C for 2 h.

Isomerization of 1-butene was carried out in a closed circulation system (reactor volume: 250 ml, catalyst: 0.2 g) with a butene initial pressure of 19 kPa at 50 °C. Prior to the reaction, a catalyst was heated in the reactor at 500 °C for 1 h under reduced pressure (0.1 Pa). The catalytic performance for the isomerization of 1-butene was evaluated by the 1st-order rate constant during the initial reaction period, and for a simultaneous side reaction of 1-butene oligomerization, forming mainly C_8 olefins by a conversion which was calculated from the pressure drop in the circulation system after the reaction had proceeded for 1 h.

An X-ray difractogram (XRD) was recorded using a Rigaku Giger Flex. A ^{31}P magic angle-spinning (MAS) NMR measurement was performed at 161.98 MHz at a spinning rate of 4 kHz with a Bruker AM-400, while H_3PO_4 was used as an external standard. Time intervals of 2 s were allowed between pulse sequences with 4 μs and 500 free induction decays were accumulated for each sample. The samples were used for the measurement without any further pretreatment.

The amount of chemisorbed ammonia was measured using a static volumetric method. Prior to adsorption, 0.5 g of the catalyst was evacuated at 500 °C for 1 h. A first adsorption of ammonia was performed at the prescribed temperature at pressures of about 1.2 kPa, followed by several repetitions of adsorption until obtaining a final pressure of 6.6 kPa. The amounts of physisorbed and chemisorbed smmonia were estimated by extrapolating the given isotherm. The physisorbed ammonia was desorbed by evacuating the sample at the same temperature as in the first adsorption for 1 h; then, only the physisorbed ammonia was measured with the second adsorption. The amount of chemisorbed ammonia was evaluated by the difference between the first and second adsorption of ammonia.

Results and Discussion

Deposition of Boron Phosphate. Figures 1 and 2 show the effects of the CVD temperature upon BPO_4 deposition for a source P/B ratio of 1. For a CVD time of 3 h or above, the BPO_4 loading exhibited a maximum at a CVD temperature of 300 °C, while the BPO_4 loading slightly increased with increasing CVD temperature for CVD times of 1 and 2 h (Fig. 1). This is related to the change in surface area of the catalyst, and is discussed later. At 300 °C, the BPO_4 loading was increased monotonously with a CVD time up to a maximum of 0.96 g g-silica^{-1} for 5 h. Such a large loading could not be realized by the impregnation method. The P/B ratio in the catalyst changed with both the CVD temperature and time (Fig. 2). At CVD temperatures below 300 °C, espe-

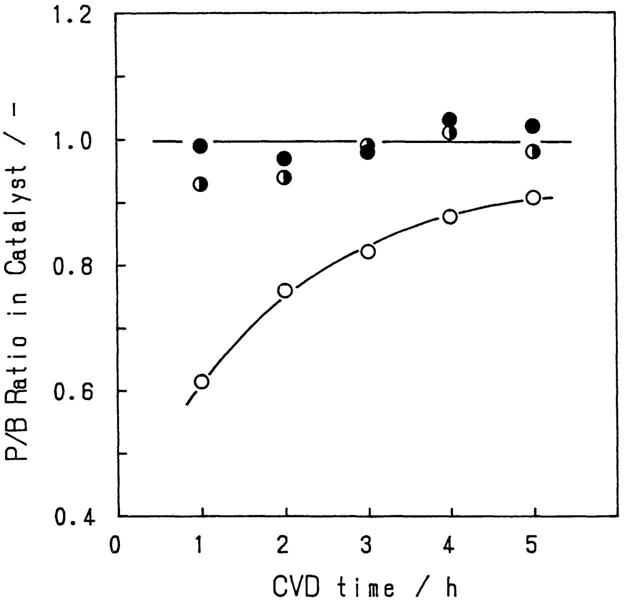

Fig. 2. Change in P/B ratio with CVD time.
○, prepared at 250 °C; ◑, 300 °C; ●, 350 °C.
P/B ratio in CVD source is 1.

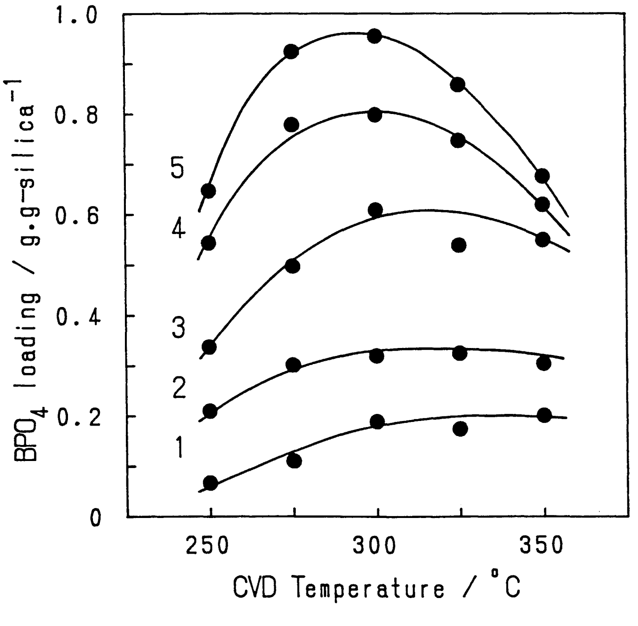

Fig. 1. Effect of CVD temparature and time on the BPO_4 deposition.
P/B ratio in CVD source is 1. Numbers show the CVD time (h).

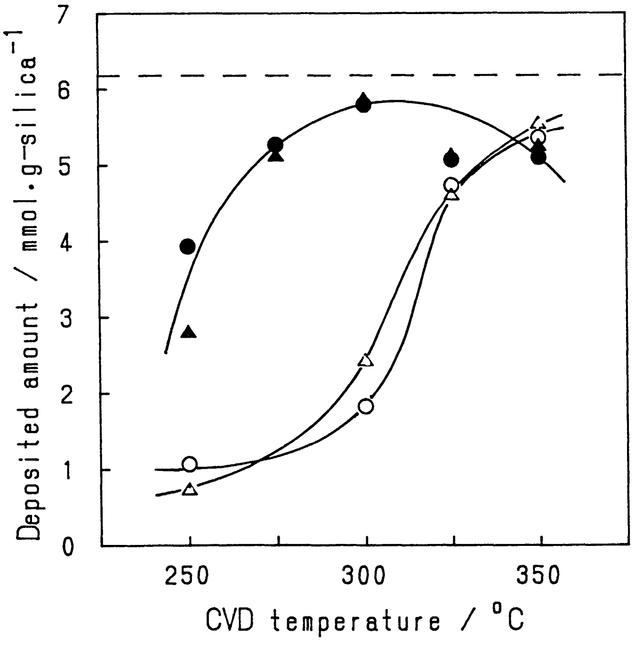

Fig. 3. Comparison of individual deposition with simultaneous deposition of B_2O_3 and P_2O_5.
○, B in B_2O_3/SiO_2; △, P in P_2O_5/SiO_2; ●, B; ▲, P in CVD BPO_4/SiO_2 (P/B=1).
Dashed line shows the maximum deposition.

cially for a short CVD time, the P/B ratio became smaller than 1. At CVD temperatures of 300 °C and above, however, the P/B ratio nearly equaled 1. Therefore, both the sufficient deposition rate and the expected P/B ratio were attained at 300 °C.

Figure 3 shows a comparison of the individual deposition with a simultaneous deposition of both the boron and phosphorus components. When either $B(OEt)_3$ or $PO(OMe)_3$ was fed individually, the deposition behavior of individual oxides was similar to each other. At a CVD temperature of 325 °C, either B_2O_3 or P_2O_5 was readily deposited on SiO_2, whereas at temperatures lower than 325 °C, the individual oxides were slowly deposited. In contrast to individual deposition, the simultaneous deposition of boron and phosphorus components satisfactorily proceeded, even at 275 °C with a P/B ratio of 1. The simultaneous supply of alkoxides drastically lowered the deposition temperature, and the deposition of BPO_4 proceeded with an excess boron component at 250 °C at which the individual oxides could hardly be deposited. Although oxygen accelerated the deposition rate of individual oxide, such as B_2O_3,[14] BPO_4 was deposited on silica even in the absence of oxygen at 300 °C. Moreover, both B_2O_3/SiO_2 and P_2O_5/SiO_2 prepared by CVD using the corresponding alkoxides at 350 °C were inactive for the isomerization of 1-butene, while the BPO_4/SiO_2 prepared at 300 °C was catalytically active. These results indicate that the deposition of BPO_4 occurred on the surface of silica with an accompanying formation of boron phosphate.

Figures 4 and 5 show the effects of the P/B ratio in the CVD source upon BPO_4 deposition. At an optimum CVD temperature of 300 °C, the BPO_4 loading almost reached the maximum deposition expressed by dashed lines for each CVD time (Fig. 4). Furthermore, the P/B ratio in the catalyst nearly equaled the source P/B ratio, whereas an excess boron component

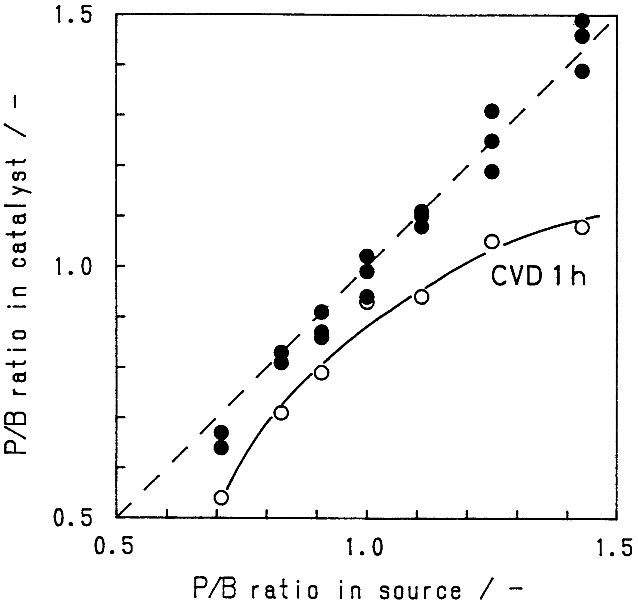

Fig. 5. Effect of P/B ratio in CVD source on P/B ratio in deposited BPO_4.
Dashed line shows the controlled composition of deposition.

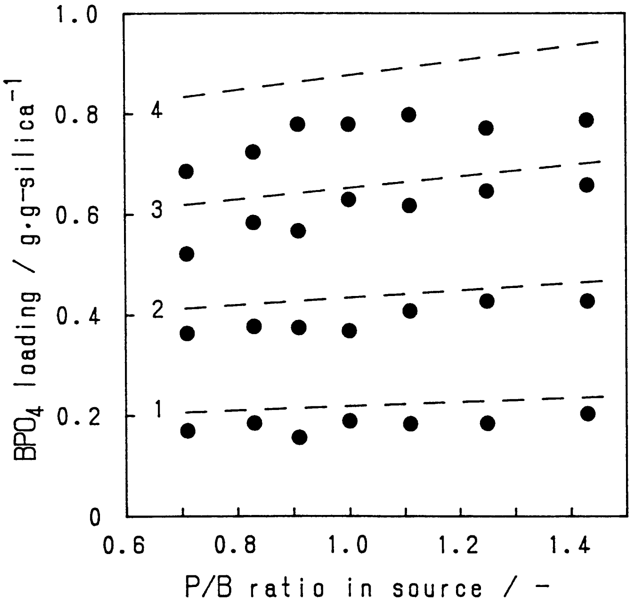

Fig. 4. Effect of P/B ratio in CVD source upon BPO_4 deposition at 300 °C.
Numbers in Figure shows the CVD time (h). Dashed line shows the maximum deposition for each CVD time.

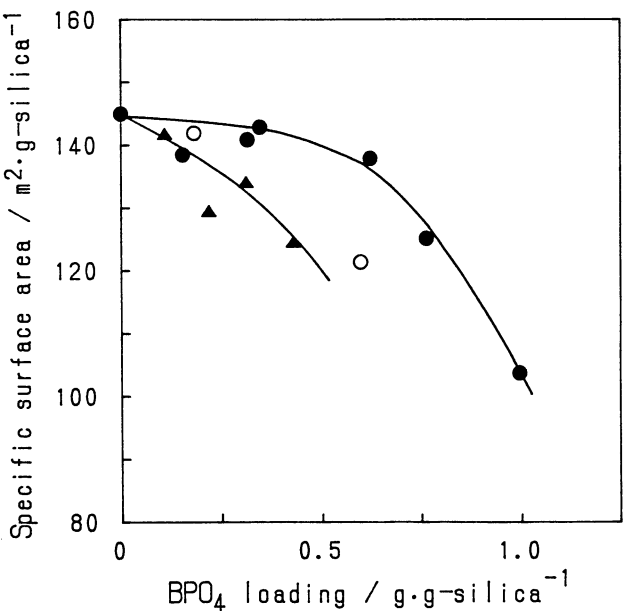

Fig. 6. Change in specific surface area with BPO_4 loading.
●, CVD BPO_4/SiO_2 prepared at 300 °; ○, at 350 °C; ▲, impregnation catalyst. The P/B ratio is 1.

was deposited for a short CVD time of 1 h (Fig. 5). Consequently, BPO_4 with the desired P/B ratio could be deposited on a silica support at 300 °C by controlling the source P/B ratio in the range between 0.7 and 1.4.

Structure of Deposited Boron Phosphate. Figure 6 shows changes in specific surface area with BPO_4 loading. For CVD BPO_4/SiO_2 catalysts prepared at 300 °C, the surface area based on the unit weight of the silica support did not change, even at a BPO_4 loading of 0.6 g g-silica^{-1}, whereas those of the impregnation catalysts linearly decreased with an increase in BPO_4 loading. Above the loading of 0.6 g g-silica^{-1}, however, it steeply decreased with an increase in BPO_4 loading. On the other hand, for CVD catalysts prepared at 350 °C, the surface area decreased with BPO_4 loading in a similar manner as those of IMP BPO_4/SiO_2 catalysts. As shown in Fig. 1, BPO_4 loading decreased at high CVD temperatures. This fact is speculated to be caused by concentrated deposition onto the entrance of the micropore of the support, followed by a closure of the micropore. These findings in Figs. 1 and 6 suggest that a uniform deposition of BPO_4 was attained at 300 °C, owing to an optimum deposition rate of BPO_4.

Figure 7 illustrates the XRD spectra of BPO_4 catalysts. An unsupported BPO_4 exhibited sharp crystalline diffraction peaks at 2θ=24.5, 40.0, and 49.0 attributed to a cristobalite-type structure[2] (Fig. 7-a). An IMP BPO_4/SiO_2 catalyst also showed the same diffraction patterns as unsupported BPO_4 with low crystallinity, even after drying at 110 °C (Fig. 7-b). None of the CVD BPO_4/SiO_2 catalysts, however, showed any diffraction peaks, indicating that the BPO_4 deposited on silica was amorphous.

The ^{31}P MAS NMR of the catalyst was measured in order to elucidate the amorphous phase of deposited BPO_4. For a P/B ratio of 1, an unsupported crystalline BPO_4 showed a sharp resonance at −29.6 ppm together with two small signals at 0.4 and −21.7 ppm (Fig. 8-a). The chemical shift at −29.6 ppm is a characteristic signal for a crystalline BPO_4, which is considered to be caused by a phosphate anion tetrahedrally coordinated by four boron atoms. An additional shift at 0.4 ppm may be attributed to a free phosphate anion, such as phosphoric acid. The silica-supported P_2O_5 had two characteristic chemical shifts at −43.9 and 0.3 ppm (Fig. 8-b). The chemical shifts of P_2O_5 are quite different from those of BPO_4.

For a P/B ratio of 1.1, the ^{31}P MAS NMR spectra of BPO_4 catalysts are shown in Fig. 9. Both the

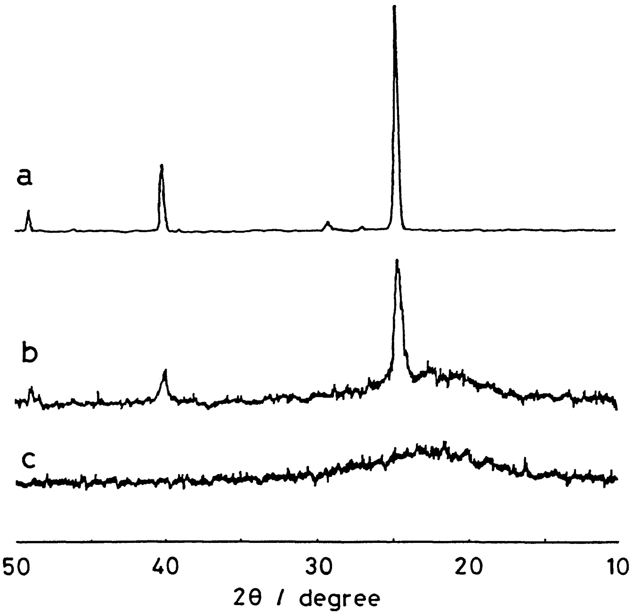

Fig. 7. XRD spectra of catalysts prepared under different conditions.
a, unsupported BPO_4 (P/B=1); b, BPO_4 (36 wt%)/SiO_2 prepared by impregnation; c, BPO_4 (36 wt%)/SiO_2 prepared by CVD.

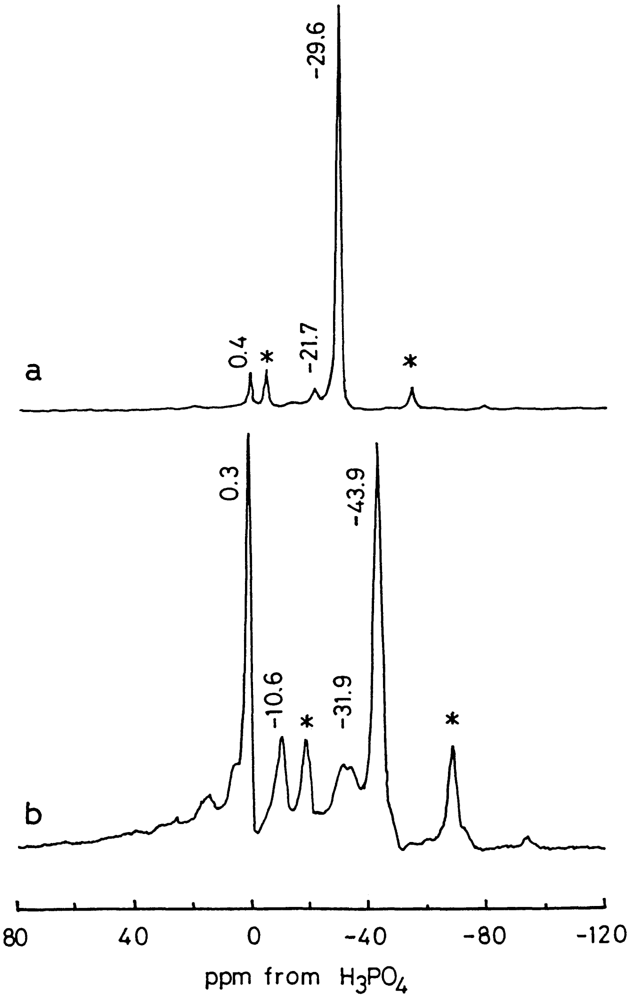

Fig. 8. ^{31}P MAS NMR spectra of phosphate catalysts.
a, unsupported BPO_4 (P/B=1); b, P_2O_5 (20 wt%)/SiO_2 prepared by impregnation.
* denotes a spinning side band.

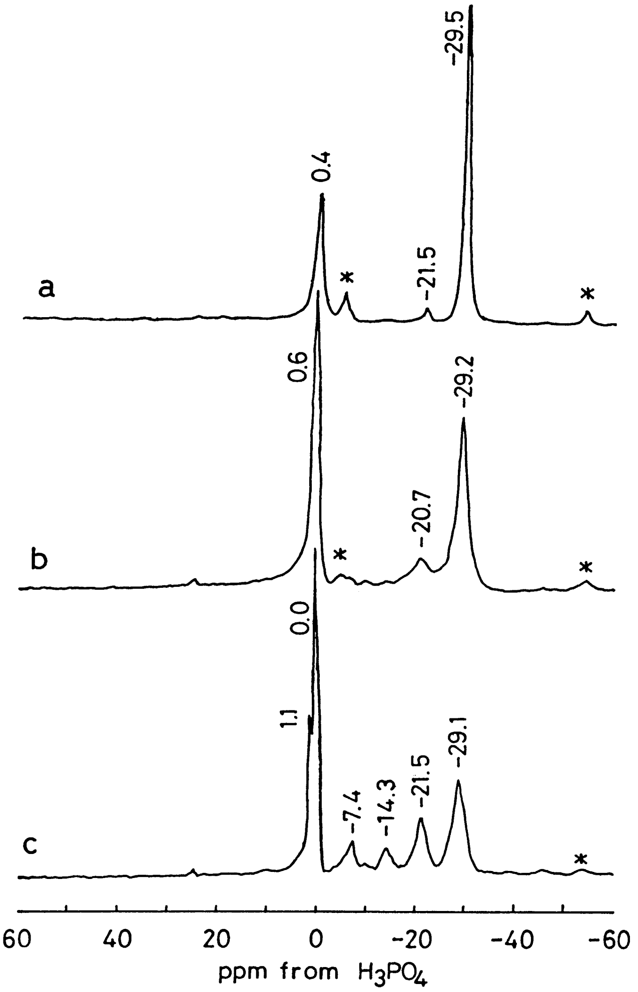

Fig. 9. ^{31}P MAS NMR spectra of BPO_4 (P/B=1.1) catalysts.
a, unsupported BPO_4; b, BPO_4 (20 wt%)/SiO_2 prepared by impregnation; c, BPO_4 (36 wt%)/SiO_2 prepared by CVD.
* denotes a spinning side band.

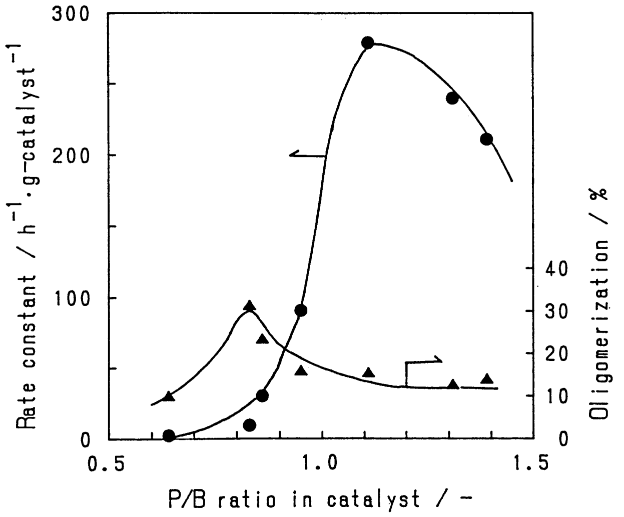

Fig. 10. Catalytic activity of CVD BPO_4/SiO_2 at 50 °C.
●, Isomerization of 1-butene; ▲, oligomerization.
CVD catalysts were prepared at 300 °C for 2 h.

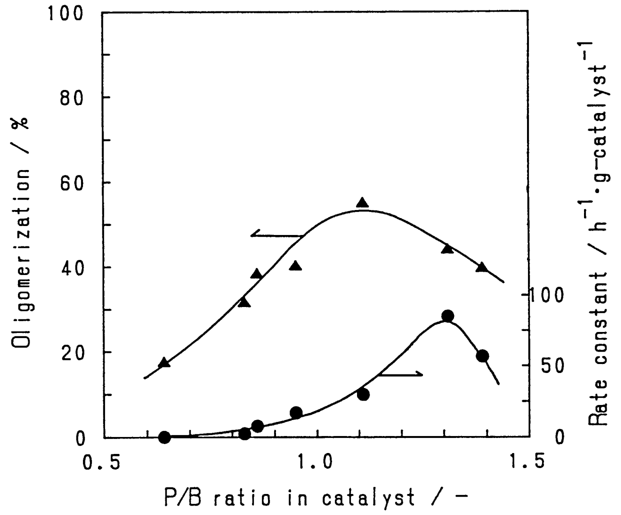

Fig. 11. Oligomerization activity of CVD BPO_4/SiO_2 at 0 °C.
Symbols as those in Fig. 10.

unsupported BPO_4 and the IMP BPO_4/SiO had three chemical shifts at −29.5, −21.5, and 0.4 ppm (Fig. 9-a and b) in similar manner as for Fig. 8-a. An increase in the phosphorus content weakened the intensity of the shift at −29.2 ppm, and strengthened that at 0.4 ppm. The CVD BPO_4/SiO_2 had two other signals at −14.3 and −7.4 ppm in addition to the above-mentioned three chemical shifts (Fig. 9-c). Further, the chemical shift at 0.4 ppm was split into two signals at 0 and 1.1 ppm. These five chemical shifts, except for that at 1.1 ppm, each appeared at about 7.2 ppm intervals between 0 and −29.1 ppm. For chemical shifts of ^{29}Si in aluminosilicates, the most characteristic trend is that substitution of the Si ions in silicate tetrahedra by Al ions leads to low-field shifts at each 4 to 6 ppm intervals.[18] The five ^{31}P chemical sifts suggest that not less than 5 different types of phosphate tetrahedra existed on the surface of the CVD BPO_4/SiO_2 catalyst. These results indicate that amorphous composite oxides, having micro-structures of BPO_4, were highly dispersed on silica for the CVD catalyst.

Catalytic Activity of CVD BPO_4/SiO_2. The catalytic activity for the isomerization of 1-butane was affected by the P/B ratio in the CVD BPO_4/SiO_2 catalyst prepared at 300 °C (Fig. 10). In the region of excess phosphorus, the activity was much higher than that in the region of excess boron, and the maximum activity was obtained at a P/B ratio near 1.1. The trans/cis ratio of product 2-butene ranged from 1.0 to 1.3 at a 1-butene conversion level of 50%, irrespective of the P/B ratio. In addition to isomerization, a small amount of butene dimers was produced with

Table 1. Acid Amount Measured by Ammonia Adsorption

BPO_4 catalyst (P/B ratio)		Content	Adsorbed amount/mmol g^{-1}	
		wt%	150 °C[a]	300 °C[a]
CVD	(1.0)	28	—	0.12
CVD	(0.83)	27	0.34	0.13
CVD	(1.1)	29	0.39	0.13
Impregnation	(1.1)	30	0.22	0.11
Unsupported	(1.1)	100	0.08	0.04

a) Adsorption temperature of ammonia.

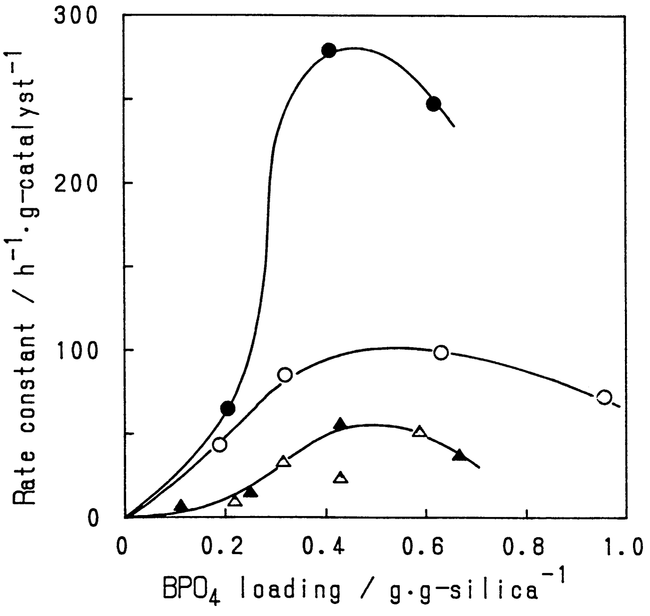

Fig. 12. Isomerization activities of various BPO_4/SiO_2 catalysts at 50 °C.
●, CVD catalyst of P/B=1.1; ○, P/B=1.
▲, Impregnation catalyst of P/B=1.1; △, P/B=1.

passing of the reaction time. The conversions of 1-butene to oligomers were 10—29% after the reaction had proceeded for 1 h. In order to clarify the catalytic behavior for oligomerization, the reaction was performed at lower temperatures. Since the isomerization activity was suppressed, the essential oligomerization activity appeared at 0 °C (Fig. 11). The maximum oligomerization activity was also observed at a P/B ratio near 1.1. This result is consistent with the catalytic behavior of unsupported BPO_4 for the liquid-phase oligomerization of 1-decene.[10)]

Figure 12 shows a comparison of CVD BPO_4/SiO_2 with the IMP BPO_4/SiO_2 catalyst regarding catalytic activity in 1-butene isomerization. For the CVD catalyst with a P/B ratio of 1, the isomerization activity increased with BPO_4 loading, passed through a maximum and then decreased above a loading of 0.6 g g-silica^{-1}. The decrease in the activity was considered to be caused by a closure of the micropore of the support, as has been described in connection with the results of the change in the specific surface area with BPO_4 loading (Fig. 6). The CVD catalysts, especially for the P/B ratio of 1.1, were much more active than both the IMP BPO_4/SiO_2 catalysts and the unsupported BPO_4 (P/B=1.1) whose rate constant for 1-butene isomerization was 89 h^{-1} g-catalys^{-1}. In addition, for the oligomerization activity, the CVD catalysts were also more active than both IMP BPO_4/SiO_2 and unsupported BPO_4 whose conversions were 6—9% at 50 °C (Fig. 10).

In order to evaluate the acid amount of catalyst, the amount of chemisorbed ammonia was measured volumetrically (Table 1). Irrespective of the P/B ratio, the amounts of ammonia chemisorbed on CVD catalysts were almost unchanged. The changes in the catalytic activity with the P/B ratio (Figs. 10 and 11) are not attributable to the acid amount, but probably to acid type (Brønsted or Lewis acid) of catalyst,[2,11)] though further work concerning the acid type and strength of CVD BPO_4/SiO_2 catalysts is in the progress. However, it has been clearly demonstrated that the acid amount of the CVD BPO_4/SiO_2 catalyst is much larger than those of both IMP BPO_4/SiO_2 and unsupported BPO_4. This tentatively explains the superiority of the CVD catalyst for the reactions mentioned above.

In conclusion, amorphous boron phosphate was deposited on a silica support with the desired P/B ratio and with high dispersion by means of a CVD method. The resulting CVD BPO_4/SiO_2 catalyst was superior to the impregnation catalyst for the isomerization of 1-butene and the simultaneous side reaction of oligomerization.

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