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OLIGOMERIZATION OF CIS-2-BUTENE WITHOUT ITS DOUBLE BOND MIGRATION OVER BORON PHOSPHATE EVACUATED AT A HIGH TEMPERATURE

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Although boron phosphate calcined in air at 1173 K did not show any catalytic activity for the isomerization and oligomerization of *cis*-2-butene at 298 K, boron phosphate evacuated at 1173 K catalyzed the oligomerization without any detectable formation of 1-butene at 273 K.

It is known that boron phosphate contains on its surface both Brönsted and Lewis acid sites and in addition that the catalytic activity is, at least in part, related to the presence of such sites.[1)] Infrared spectroscopic studies show that the effect of evacuation at different temperatures alters the surface properties of boron phosphate.[2)] There are, however, no earlier studies of the catalytic properties of boron phosphate evacuated at elevated temperatures. It therefore appeared to be of interest to examine the catalytic activity and selectivity of high-temperature evacuated boron phosphate for the isomerization and oligomerization of *cis*-2-butene.

Boron phosphate was prepared by the reaction of H_3BO_3 with H_3PO_4 (1:1 in molar ratio) at 353 K and was subjected to drying at 373 K for 24 h, heating at 523 K for 2 h, and then evacuating *in situ* at 523-1273 K for 2 h. X-Ray diffraction analyses showed that all pretreated catalysts were BPO_4. All catalytic tests were carried out in a closed circulation reactor (*ca*. $5.2 \times 10^{-4} m^3$) with an initial pressure of 9.3 kNm^{-2} of *cis*-2-butene over 0.2 g of catalyst at 273 K. Products were analyzed by gas chromatography and mass spectrography.

When 0.2 g of boron phosphate evacuated at 1173 K was used, 55% *cis*-2-butene was converted to a mixture of C_8 and C_{12} hydrocarbons at 273 K in 0.5 h. On the other hand, boron phosphate calcined in air at 1173 K showed neither catalytic activity for the oligomerization nor that for the isomerization even at 298 K. In the Figure, the amount (mol%) of *trans*-2-butene and 1-butene isomerized from *cis*-2-butene, and the extent (%) of a decrease in the total pressure at the initial stage of the reaction are shown as a function of evacuation temperature. Catalytic activities in both the isomerization and the oligomerization are beginning to appear following evacuation at 573 K and increase to maxima at 773 K,

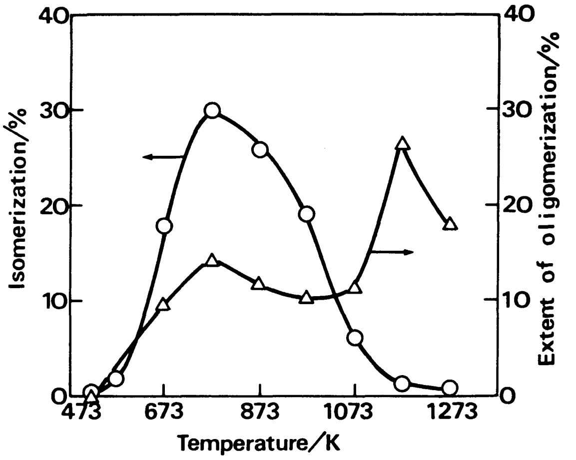

Fig. Isomerization and oligomerization of *cis*-2-butene over BPO_4 at 273 K. Reaction time was 5 min.

Table 1. Product distribution of butene isomers

Butene isomer	Evacuation temperature (K)							Equilibrium composition a)
	673	773	873	973	1073	1173	1273	
1-butene	4.5	4.5	4.5	2.0	0.5	0.0	0.0	1.9
trans-2-butene	35.5	35.5	35.5	38.0	39.5	40.0	40.0	77.4
cis-2-butene	60.0	60.0	60.0	60.0	60.0	60.0	60.0	20.7

a) Calculated using equilibrium constants3).

Table 2. Isomerization and oligomerization of _cis_-2-butene at 273 Ka)

Catalyst	Evacuation temperature (K)	Isomerization (%)			Oligomerization (%)
		1-butene	_trans_-2-butene	_cis_-2-butene	
BPO_4	773	3.9	60.3	35.8	37
	1173	0.0	8.2	91.8	60
Solid phosphoric acid	523	0.2	0.3	99.5	4
	773	1.6	4.8	93.6	6
	1173	1.3	4.9	93.8	3
SiO_2-Al_2O_3	773	2.0	13.4	84.6	27
	1173	0.2	1.1	98.7	23

a) Reaction time, 1 h.

above which isomerization activity decreases monotonously, while oligomerization activity passes through the minimum at 973 K and attains the other maximum at 1173 K. These activity changes were reproduced. Table 1 shows the product distribution for _cis_-2-butene isomerization (at 40% isomerization) over boron phosphate evacuated at different temperatures. The amount of 1-butene produced with boron phosphate evacuated at 673-973 K are about twice of the equilibrium value. With an increase in the evacuation temperature above 1073 K, however, the amount of 1-butene decreases progressively and reaches to zero at 1173 and 1273 K. This fact suggests that it has become feasible over boron phosphate evacuated above 1173 K to obtain an oligomer of 2-butene alone instead of an oligomer of mixtures of 2-butene and 1-butene.

Table 2 summarizes the results for the isomerization and oligomerization of _cis_-2-butene over 0.2 g of the three kinds of the catalysts; boron phosphate, solid phosphoric acid (phosphoric acid mounted on diatomaceous earth, Nikki Chemical N501), and silica-alumina (Nikki Chemical N631(L)). Contrary to expectation, solid phosphoric acid, which has been extensively used as an acid catalyst for the oligomerization of olefins, the alkylation of certain aromatic compounds, etc., showed poor activities for both the oligomerization and isomerization under the reaction conditions of this experiment. Silica-alumina was fairly effective catalyst for the oligomerization, but the ensuing formation of 1-butene was not suppressed completely. In conclusion, the present results demonstrate that boron phosphate evacuated at 1173 K is an effective and characteristic catalyst for 2-butene oligomerization.

References
1) J. B. Moffat, Catal. Rev., 18, 199 (1978).
2) J. B. Moffat and J. F. Neeleman, J. Catal., 34, 376 (1974).
3) E.F. Meyer and D. G. Stroz, J. Am. Chem. Soc., 94, 6344 (1972).

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