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Boron Phosphate as a Highly Active Catalyst for 1-Decene Oligomerization

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The oligomerization of 1-decene was studied over six kinds of solid acid catalysts involving boron phosphate. Among them evacuated boron phosphate exhibited the highest oligomerization activity: superior to not only SiO_2-Al_2O_3 but also a solid superacid, SO_4^{2-}/ZrO_2.

Recently much efforts to develop new solid acid catalysts have been made in order to convert homogeneously catalyzed processes to heterogeneously catalyzed ones, since the processes employing homogeneous catalysts such as H_2SO_4, $AlCl_3$, and BF_3 have faced several practical problems: separation of a catalyst, corrosion of a reactor, and high cost of a catalyst. As one of the processes to be substituted, the oligomerization reaction of C_8-C_{12} α-olefins is important in the production of a base oil for a synthesized lubricating oil.$^{1)}$ Previously we have found that $BPO_4$$^{2)}$ evacuated at a high temperature showed marked activity for 2-butene oligomerization.$^{3)}$ In this paper we wish to report boron phosphate as a promising catalyst for 1-decene oligomerization.

Boron phosphate was prepared by heating a mixture of H_3BO_3 and H_3PO_4 at 40 °C in a rotary evaporator, followed by drying in situ at 40 °C under 17 Torr, heating at 150 °C for 24 h, and finally calcining at 360 °C for 12 h. X-ray diffraction analyses showed that cristobalite-form of BPO_4 was involved in the resulting catalysts. The reaction was carried out at 150 °C for 5 h, unless otherwise stated, in a stirred batch reactor under inert atmosphere. A 0.2 g of catalyst was activated in situ by evacuating at various temperatures for 2 h. 1-Decene(Tokyokasei Inc.) was degassed by three freeze-pump-thaw cycles and collected into a reactor by vapor transfer by 2 cm^3(liquid). Products were analyzed by using a gas chromatograph equipped with a temperature program unit(Silicone OV-101,1 m,100-300 °C,5 °C min^{-1}).

Table 1. 1-Decene Oligomerization over BPO_4 Evacuated at Various Temperatures

Evac. temp °C	Conv. %	Compo. of oligomers /% di	tri	tetra	penta
400	79.1	63.8	29.0	7.2	0.0
500	84.1	57.5	31.8	9.2	1.5
600	86.7	58.6	33.2	8.2	0.0
700	73.1	68.2	25.9	5.9	0.0

The oligomerization activity of BPO_4 catalyst was altered by the pretreatment conditions. When evacuated at 500 °C, the conversion of 1-decene was observed to be 84.1%, while pretreated in air at 500 °C, the conversion was limited to 56.5%. As is seen in Table 1, the activity of BPO_4 is also affected by its evacuation temperature. With the rise of reaction temperature, fractions of trimer, tetramer, and pentamer increased considerably although conversions were almost unchanged (not shown). For example, at 105 °C the conversion and the total fraction of the oligomers from trimer to pentamer were 83% and 28%, respectively, while at 150 °C, 84% and 42%.

The time-course of the oligomerization over BPO_4 evacuated at 500 °C, is shown in Fig. 1, where the composition values plotted against each reaction time were obtained from a separate run using the same but fresh catalyst in each case. The reactant 1-decene decreases exponentially, while the dimer goes through a maximum of about 50% followed by the formation of the trimer, tetramer, etc. This result indicates that 1-decene oligomerization occurs consecutively; besides the dimerization proceeds faster than further growth-reactions of the dimer.

Catalytic properties of BPO_4 are compared with those of five kinds of solid acid catalysts in Table 2. Contrary to expectation, SO_4^{2-}/ZrO_2 4) which is known to be a solid superacid does not exhibit much higher activity than BPO_4. In addition, activity of BPO_4 is superior to that of silica-alumina which possesses both stronger acid sites and larger surface area. In view of the facts that the activity of alumina-boria 5) is comparable to that of silica-alumina, and alumina is less active, acid sites with acid strength Ho $\leqq$ -5.6 are considered to be active sites for this reaction. The low activities of two kinds of zeolites, H-ZSM-5 and clinoptilolite 6) could be explained by a diffusion limitation in small pores.

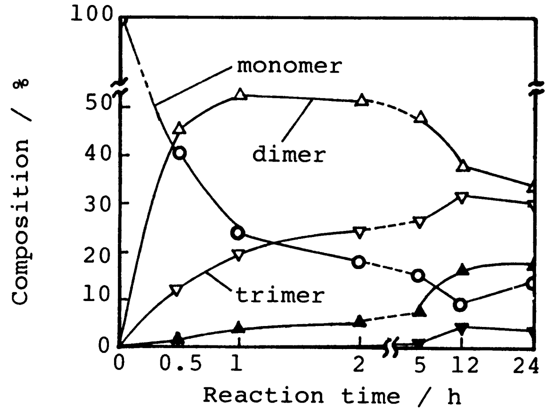

Fig. 1. Composition vs. reaction time. ▲:tetramer, ▼:pentamer.

Table 2. Catalytic and Surface Properties of Various Catalysts

Catalyst	Conv. / %	Max. acid strength/Ho	Surface area/$m^2 \cdot g^{-1}$
BPO_4	83.2	-5.6	17
SO_4^{2-}/ZrO_2	83.0	-16.04	-
SiO_2-Al_2O_3	63.3	-8.2	418
Al_2O_3-B_2O_3	69.7	-5.6	250
clinoptilolite	1.9	-5.6	170
H-ZSM-5	4.9	-5.6	-
Al_2O_3	0.4	-3.0	110

As an additional attempt to improve the catalytic properties of BPO_4, non-stoichiometric boron phosphates were also examined. The results showed that the catalyst with P/B = 1.1 was more active(91.4%) than stoichiometric boron phosphate. The details of catalytic properties of non-stoichiometric boron phosphates will be reported elsewhere.

References

1) A. Mitutani, Shokubai(Catalyst), 25, 86 (1983).
2) The term "BPO_4" hereafter represents stoichiometric boron phosphate.
3) Y. Imizu, S. Aoyama, H. Itoh, and A. Tada, Chem. Lett., 1981, 1455.
4) M. Hino and K. Arata, J. Chem. Soc., Chem. Commun., 1980, 851.
5) Y. Izumi and T. Shiba, Bull. Chem. Soc. Jpn., 37, 1797 (1964).
6) H. Sakoh, M. Nitta, and K. Aomura, Appl. Catal., 16, 249 (1985).

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