Shape-selective isopropylation of biphenyl over a highly dealuminated mordenite: effect of propylene pressure

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Received 20 January 1993; accepted 26 May 1993

A highly dealuminated H-mordenite (H-M) catalyzed the selective isopropylation of biphenyl to 4,4′-diisopropylbiphenyl (4,4′-DIPB). The high selectivity is ascribed to the shape-selective catalysis in mordenite pores. The selectivity of 4,4′-DIPB decreased during the isopropylation of biphenyl due to isomerization of 4,4′-DIPB under low propylene pressure. The increase of propylene pressure suppressed the isomerization in the isopropylation. 4,4′-DIPB itself was isomerized over highly dealuminated H-M under low propylene pressure.

Keywords: Biphenyl; 4,4′-diisopropylbiphenyl; highly dealuminated H-mordenite; shape-selective isopropylation; isomerization

1. Introduction

Shape-selective alkylation using zeolite is a useful way to introduce functional groups symmetrically to aromatic hydrocarbons. One important development on the shape-selective catalysis achieved recently is the success in selective isopropylation of biphenyl and naphthalene over H-mordenite (H-M) [1–7]. It demonstrates the effectiveness of zeolite in catalyzing the reaction of polynuclear aromatics. However, the mechanism of the catalysis related to solid acid sites and steric requirement in zeolite pores has not been fully understood. In this paper, we examine the isopropylation of biphenyl and the isomerization of 4,4′-diisopropylbiphenyl over a highly dealuminated H-M, and discuss the mechanism of the catalysis.

2. Experimental

The highly dealuminated H-M ($Si/Al_2 = 220$) was obtained from TOSOH Cor-

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poration, Tokyo, Japan, and calcined in air at 450°C just before the reaction. The isopropylation of biphenyl was carried out by using a 200 ml SUS 316 autoclave. Propylene was used as alkylating reagent. The autoclave containing biphenyl and H-M was purged with N_2 before heating. After reaching to the reaction temperature, the autoclave was supplied with propylene and kept at a constant pressure throughout the reaction. A standard set of isopropylation conditions included: biphenyl 200 mmol, H-M 2g, propylene pressure 10 kg/cm^2, and reaction temperature 250°C. The isomerization of 4,4′-DIPB was examined under the following conditions: 4,4′-DIPB mmol, H-M 1 g, propylene pressure 0–10 kg/cm^2, reaction temperature 250°C, and reaction period 4 h. The product was analyzed with a HP-5890 GC equipped with a 25 ml Ultra-1 capillary column, and identified with a HP-5978 GC-MS.

3. Results and discussion

Fig. 1 shows the course of the isopropylation of biphenyl over H-M under 10 kg/cm^2 of propylene pressure. At the early stage of the reaction, biphenyl was con-

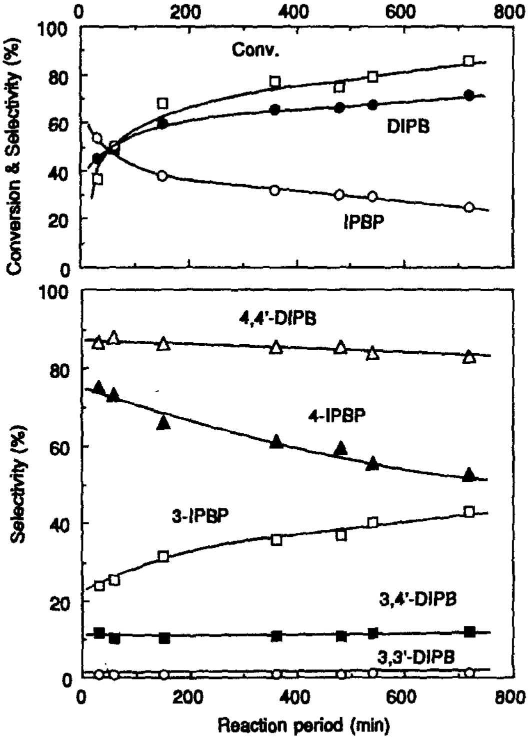

Fig. 1. Isopropylation of biphenyl over dealuminated H-mordenite. Biphenyl: 200 mmol; H-M: 2 g; propylene pressure: 10 kg/cm^2; 250°C.

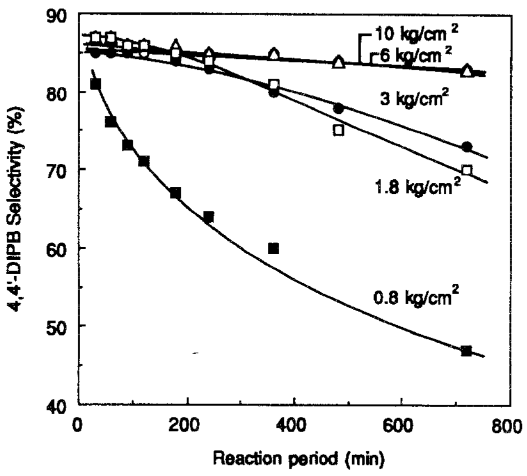

Fig. 2. Effect of propylene pressure on the isopropylation of biphenyl. Biphenyl: 200 mmol; H-M: 2 g; 250°C.

verted to isopropylbiphenyl (IPBP) isomers, especially to 4-IPBP. Diisopropylbiphenyl (DIPB) isomers increased with the consumption of IPBP isomers. The formation of 4,4′-DIPB was highly selective throughout the reaction. The selectivity of 4-IPBP decreased with increasing that of 3-IPBP. These facts indicate that the isopropylation of biphenyl to 4,4′-DIPB proceeded by a consecutive reaction mechanism via 4-IPBP. In the first stage, biphenyl was converted to a mixture of IPBP isomers, in which 4-IPBP was predominant. In the second stage, the alkylation of 4-IPBP, the most slim isomer, gave 4,4′-DIPB regioselectively. The high selectivity of 4-IPBP and 4,4′-DIPB in the isopropylation is ascribed to shape-selective catalysis by H-M pores. 3-IPBP hardly participated in further isopropylation to DIPB isomers in H-M pores because it is bulkier than 4-IPBP. These results are consistent with the negligible formation of higher products such as triisopropylbiphenyls (TrIPB) because the formation of them was restricted by H-M pores.

Fig. 2 shows the effect of propylene pressure on the selectivity of 4,4′-DIPB. The selectivity was higher than 80% in the early stage of isopropylation in all cases. The formation of 4,4′-DIPB was highly selective under high propylene pressures throughout the reaction. However, the selectivity of 4,4′-DIPB decreased significantly with reaction time under low pressures such as 0.8 kg/cm^2 [#1]. The decrease of the selectivity of 4,4′-DIPB was accompanied by increasing selectivity of 3,4′-DIPB. These results show that the propylene pressure is an important factor for the shape-selective formation of 4,4′-DIPB.

To understand the effect of propylene pressure on decreasing selectivity of 4,4′-DIPB for the isopropylation, the stability of 4,4′-DIPB over H-M was examined.

[#1] The decrease of the selectivity of 4,4′-DIPB was described shortly in patent publications [5,6].

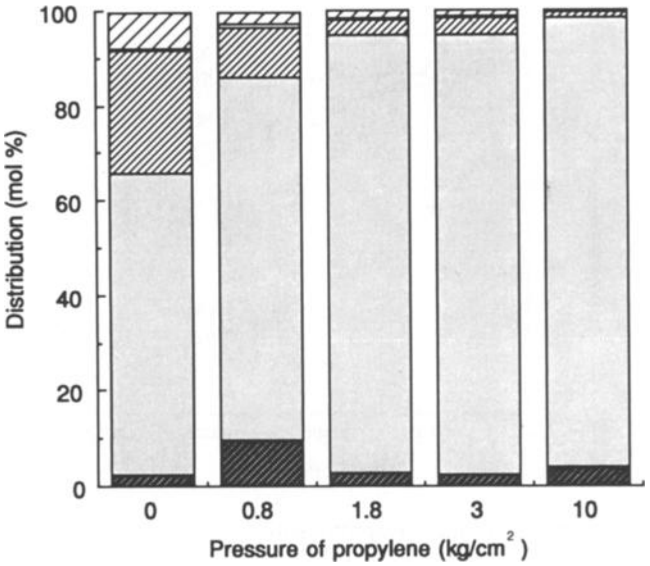

Fig. 3. Effect of propylene pressure on the isomerization of 4,4′-DIPB. 4,4′-DIPB: 100 mmol; H-M: 1 g; 250°C, 4 h. (▨) IPBP; (⊟) 3,3′-DIPB; (▩) 3,4′-DIPB; (▤) 4,4′-DIPB; (▩) TrIPB.

As summarized in fig. 3, the high extent of isomerization of 4,4′-DIPB to 3,4′-DIPB was observed under propylene pressure below 0.8 kg/cm^2. However, the isomerization was negligible under high pressures such as 10 kg/cm^2. The reaction occurs likely on the external acid sites because the isomerized products hardly accomodate in H-M pores by steric restriction. Propylene prevents the isomerization probably due to preferential adsorption on acid sites. From the above discussion, it is concluded that the decrease of the selectivity of 4,4′-DIPB in the isopropylation of biphenyl at low propylene pressure occurs by the isomerization of 4,4′-DIPB, not by the decrease of shape-selective catalysis. The low formation of TrIPB in the isomerization of 4,4′-DIPB supports that the alkylation occurs in H-M pores by shape-selective catalysis, and that TrIPB hardly accomodates in the H-M pores. The relatively high formation of TrIPB under 0.8 kg/cm^2 propylene pressure likely proceeded by the isopropylation of 3,4′-IPBP on acid sites of the external surface.

In summary, the highly dealuminated H-M gives highly selective formation of 4,4′-DIPB for the isopropylation of biphenyl. The increase of propylene pressure suppresses the isomerization of 4,4′-DIPB to maintain the high selectivity for the isopropylation. The isomerization occurs likely on acid sites of the external surface, and the isomerized products hardly accommodate in H-M pores by steric restriction. Propylene prevents the isomerization probably due to its preferential adsorption on acid sites.

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