

# The alkylation of biphenyl over three-dimensional large pore zeolites: The influence of zeolite structure and alkylating agent on the selectivity for 4,4'-dialkylbiphenyl

Yoshihiro Sugi<sup>a,\*</sup>, Hiroyoshi Maekawa<sup>a</sup>, Yukio Hasegawa<sup>a</sup>, Akira Ito<sup>a</sup>, Ryota Asai<sup>a</sup>,  
Daisuke Yamamoto<sup>a</sup>, Kenichi Komura<sup>a</sup>, Yoshihiro Kubota<sup>a,1</sup>,  
Jong-Ho Kim<sup>b</sup>, Gon Seo<sup>b</sup>

<sup>a</sup> Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Gifu 501-1193, Japan

<sup>b</sup> School of Applied Chemical Engineering, The Research Institute for Catalysis, Chonnam National University, Gwangju 500-757, Republic of Korea

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## Abstract

Catalytic properties of three-dimensional zeolites, Y (FAU), Beta (BEA), and CIT-1 (CON) zeolites were examined in the alkylation, isopropylation, *sec*-butylation, and *tert*-butylation, of biphenyl (BP), and compared to those of H-mordenite (MOR). The selectivities for 4,4'-dialkylbiphenyl (4,4'-DABP) varied with the types of zeolite and of alkylating agent. FAU, BEA, and CON gave only low selectivities for 4,4'-diisopropylbiphenyl (4,4'-DIPB) in the isopropylation, and predominant isomers were bulky and thermodynamically unstable 2,2'-, 2,3'-, and 2,4'- at lower temperatures, and bulky and thermodynamically stable 3,4'- and 3,3'-DIPB at higher temperatures: this is quite different from catalytic features over MOR, which gave 4,4'-DIPB with high selectivities at moderate temperatures. These results suggest that FAU, BEA, and CON have no shape-selective nature in the isopropylation, and that the reaction is principally controlled kinetically at lower temperatures, and thermodynamically at higher temperatures. The *sec*-butylation gave similar results to the isopropylation. Although the selectivities for 4,4'-di-*sec*-butylbiphenyl (4,4'-DSBB) were higher than those in the isopropylation, predominant isomers were 2,2'-DSBB (2,2'-, 2,3'-, and 2,4'-) at lower temperatures, and 3,4'- and 3,3'-DSBB at higher temperatures. The *tert*-butylation gave 4,4'-di-*tert*-butylbiphenyl (4,4'-DTBB) in moderate to high selectivities over all zeolites at moderate temperatures: the selectivity for 4,4'-DTBB was higher than 80% over BEA and CON; however, it still remained at 50% over FAU. FAU channels with super cages are too large for selective formation of 4,4'-DTBB.

From these results, it is concluded that the selectivity for 4,4'-DABP in the alkylation over MOR, FAU, BEA, and CON is determined by the exclusion of bulky isomers at their transition states, and that the exclusion is caused by the steric restriction at the transition states of bulky isomers by the zeolite channels.

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## 1. Introduction

Shape-selective catalyses by zeolites occur by differentiating reactants, products, and/or reaction intermediates according to their shape and size in sterically restricted environment of the zeolite [1–4]. Only molecules of which dimensions are less than

the pore size of the zeolite can enter their channel, and react at internal catalytic sites. Bulky molecules are excluded from the channels, resulting in the formation of the slim isomers, and only molecules which can diffuse through the channels will appear in the products. On the other hand, if the spaces of zeolite channels are large enough to accommodate the reactant and/or the products, or if the reactants and the products are smaller than the spaces inside the channels, the reaction is controlled kinetically due to the reactivity of each position at lower temperatures, and to the thermodynamic stability of the products at higher temperatures [1–6]. These considerations indicate that the extent of the exclusion of bulky molecules

\* Corresponding author.

E-mail address: [ysugi@gifu-u.ac.jp](mailto:ysugi@gifu-u.ac.jp) (Y. Sugi).

<sup>1</sup> Current address: Department of Materials Science and Engineering, Graduate School of Engineering, Yokohama National University, Yokohama 240-8501, Japan.

from the channels is one of key factors for shape-selective catalysis by zeolites, and that it depends on the types of zeolite and of alkylating agent.

The isopropylation of biphenyl (BP) is a typical acid-catalyzed reaction for demonstrating shape-selective nature of zeolite [4–29]. Selective formation of the least bulky 4,4'-diisopropylbiphenyl (4,4'-DIPB) should be facilitated over zeolites if the catalytic sites are sterically restricted. In previous papers, we described that 4,4'-DIPB was selectively obtained from BP over dealuminated H-mordenite (MOR) [4,6–13]. The high selectivity for 4,4'-DIPB suggests that catalytically active sites in MOR channels effectively exclude the transition state of bulky isomers from the channels, resulting in selective formation of the least bulky 4,4'-DIPB. On the other hand, many of large pore zeolites, such as Y, Beta, and L zeolites, gave mixtures of DIPB isomers, and the selectivities for 4,4'-DIPB over these zeolites were much lower than those over MOR [5,6]: these results are due to the large reaction spaces in their channels. However, there have been several works that shape-selective formation of 4,4'-di-*tert*-butylbiphenyl (4,4'-DTBB) occurred if 2-methyl-2-propanol or 2-methylpropene was used as alkylating agent [16–19]. These results prompted us to study how zeolite structure, particularly, dimensionality, pore size, and channel structure, affects on the catalysis, and how bulkiness of alkylating agent influences transition states leading to shape-selective catalysis in zeolite channels.

In this paper, we describe the alkylation, *i.e.*, isopropylation, *sec*-butylation, and *tert*-butylation, of BP over some three-dimensional zeolites, Y (FTC: FAU; 12-12-12 channels with super cages), Beta (FTC: BEA; 12-12-12 channels), and CIT-1 (FTC: CON; 12-12-10 channels) [30] from points of view how zeolite structure and bulkiness of alkylating agents affect shape-selective catalysis in their channels. The discussion in the paper is based on the selectivity for dialkylbiphenyl (DABP) isomers.

## 2. Experimental

### 2.1. Zeolites

Beta and CIT-1 zeolites were synthesized according to the literatures [31,32]. Mordenite ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 128$ ; TSZ-690HOA; Tosoh Corp., Tokyo, Japan) and Y zeolite ( $\text{SiO}_2/$

$\text{Al}_2\text{O}_3 = 30$ ; CBVZ720, Zeolyst CV, Groningen, The Netherlands) were obtained commercially. All zeolites were used as acidic form in the catalytic reactions.

The structures and properties of zeolites have been characterized by FE-SEM, XRD, ICP analysis,  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR,  $\text{N}_2$  adsorption, and  $\text{NH}_3$ -TPD. Table 1 summarizes typical properties of the zeolites in this study. Some of results of the characterization of zeolites are also shown in Figs. S1–S5 in supplementary data. The abbreviation of the type of zeolite is expressed by framework type code (FTC) from the IZA Structure Commission [30].

### 2.2. The alkylation of BP

The alkylation of BP was carried out in a 100-ml SUS-316 autoclave under the pressure of propene, 1-butene, or 2-methylpropene. Typical conditions of the isopropylation were: BP 7.71 g (50 mmol), catalyst 0.25 g, reaction temperature 150–250 °C, and 4 h of operating period under 0.8 MPa of propene pressure (0.4 MPa for 1-butene in the *sec*-butylation and for 2-methylpropene in the *tert*-butylation). An autoclave containing BP and the catalyst was purged with nitrogen before heating. After reaching the reaction temperature, propene was introduced into the autoclave, the reaction was started with agitation, and the pressure maintained constant throughout the reaction. After cooling the autoclave, the catalyst was filtered off, and washed well with toluene. Combined liquid bulk products were diluted with toluene, and subjected to analysis by using a gas chromatograph GC-14A (Shimadzu Corp., Kyoto, Japan) equipped with an Ultra-1 capillary column (25 mm  $\times$  0.2 mm; Agilent Technologies, Inc., MA, U.S.A.). The products were also identified by using a Shimadzu gas chromatograph–mass spectrometer GC–MS 5000 using the Ultra-1 capillary column as shown above.

The yields of each product are calculated on the basis of the amount of starting BP, and the selectivities for each alkylbiphenyl (ABP) and dialkylbiphenyl (DABP) isomers are expressed based on total amounts of ABP and DABP isomers, respectively.

Selectivity for a DABP (ABP) isomer (%)

$$= \frac{\text{Each DABP (ABP) isomer (mol)}}{\text{DABP (ABP) isomers (mol)}} \times 100$$

Table 1  
Properties of zeolites

Zeolite	Topology (FTC)	Dimension	Pore system	Pore opening (nm)	$\text{SiO}_2/\text{Al}_2\text{O}_3$	Surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{mL}/\text{g}$ )	$\text{NH}_3$ -TPD peak temperature (°C)	Acid amount ( $\text{mmol}/\text{g}$ )	Note
Mordenite	MOR	2	12-8	0.65 $\times$ 0.70 (0 0 1) <sup>a</sup> 0.34 $\times$ 0.48 (0 1 0)	128	460	0.16	389	0.20	Side pocket (8MR:0.26 $\times$ 0.57)
Y	FAU	3	12-12-12	0.74 $\times$ 0.74 (1 1 1)	30	810	0.29	254	0.18	Super cage
Beta	BEA	3	12-12-12	0.66 $\times$ 0.77 (1 0 0) 0.56 $\times$ 0.56 (0 0 1)	111	660	0.28	304	0.18	
CIT-1	CON	3	12-12-10	0.64 $\times$ 0.70 (0 0 1) 0.59 $\times$ 0.70 (1 0 0) 0.45 $\times$ 0.51 (0 1 0)	40	538	0.22	303	0.23	

<sup>a</sup> Plane index.

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