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Shape-Selective Isopropylation of Aromatic Hydrocarbons over H-Mordenite in Supercritical Carbon Dioxide Medium

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The isopropylation of aromatic hydrocarbons isobutylbenzene (IBB), naphthalene (NP), and biphenyl (BP) was examined over H-mordenite (MOR), H-β (BEA), and H-Y (FAU) zeolites in supercritical carbon dioxide (*sc*-CO_2) medium. MOR was only selective for the formation of the least bulky 4-isobutylcumene (4-IBC) in the isopropylation of IBB. In particular, the catalytic activity and selectivity for 4-IBC were enhanced by the dealumination of MOR; MOR with 110 of SiO_2/Al_2O_3 ratio rendered the highest performance; however, the catalytic activity was decreased by further dealumination. Thermogravimetric analyses confirmed the reduction of coke formation on the catalysts in *sc*-CO_2 medium, preventing the deactivation of MOR. Shape-selective formation of the least bulky isomers, 2,6-diisopropylnaphthalene (2,6-DIPN) and 4,4′-diisopropylbiphenyl (4,4′-DIPB), was also observed in the isopropylation of NP and BP over MOR in *sc*-CO_2. *sc*-CO_2 works as an efficient medium to access and/or replace substrates and their products to/from acidic sites in the MOR channels. In particular, the removal of coke precursors from acidic sites on the zeolite is enhanced by the *sc*-CO_2 medium, resulting in decreased coke formation.

Zeolite-catalyzed shape-selective catalysis is a promising way to synthesize symmetrically substituted isomers for industrial chemicals and advanced materials.[1–9] Shape-selective catalysis occurs to form the least bulky isomer because the zeolite pores prevent the formation of bulkier isomers.[1–6] Types of zeolite, adjustment of pore radii and acidity, and/or deactivation of external acid sites are all key factors for the enhancement of shape-selective catalysis.[1,2,4–6]

In general, solid acid catalysts such as zeolites with confined micropores suffer deactivation due to coke formation on the active sites of the catalysts.[10–12] Therefore, one of the most important challenges for green catalytic processes is to minimize coke formation by controlling diffusion of reactant(s), product(s), and coke-precursors from active sites.

Supercritical fluids, such as supercritical CO_2 (*sc*-CO_2), have become more attractive media for chemical reactions. They offer enhanced solubility of reactants, products, and coke-precursors, faster heat transfer from catalysts to dense gases, and easier product separation from the catalysts, by tuning pressure and temperature.[13–15] Moreover, higher molecular weight carbon-rich compounds such as polynuclear aromatic hydrocarbons are soluble in the reaction conditions due to the high density and low viscosity of *sc*-CO_2, resulting in minimizing catalyst deactivation. All of these reasons have established *sc*-CO_2 as an attractive choice for some reactions, such as solid acid catalysis.[16–23]

In this paper, we report the isopropylation of isobutylbenzene (IBB) to isobutylcumene (IBC) isomers in *sc*-CO_2 medium, where 3- and 4-IBCs are important precursors for the synthesis of antioxidants, pharmaceuticals, fragrances, and other fine chemicals.[24–27] In particular, we emphasize our results on dealuminated H-mordenite (MOR) catalysts and the impact of *sc*-CO_2 medium for achieving higher conversion, and, more importantly, higher selectivity for 4-IBC. We also studied the isopropylation of polynuclear aromatic hydrocarbons, naphthalene (NP) and biphenyl (BP) to elucidate shape-selective catalysis in *sc*-CO_2 medium over MOR.

Experimental

Zeolites. H-Mordenites (MOR(10), MOR(26), MOR(73), MOR(110), MOR(128), and MOR(230))[28] and H-ZSM-5 (MFI(54)) obtained as the NH_4-form) were obtained from TOSOH Corporation, Tokyo, Japan. H-Y (FAU(30) and FAU(80)) and H-β (BEA(26)) zeolites were obtained from Zeolyst International, PA, USA. ZSM-11 (MEL(49)) zeolite was obtained from N. E. CHEMCAT Corporation, Tokyo, Japan. BEA(100) was synthesized according to the literature.[29] All zeolites were calcined at 550 °C in air for 6 h prior to use.

Isopropylation in *sc*-CO_2. The isopropylation was carried out in a 100 mL SUS-316 autoclave (equipped with an agitator) using dry ice as the source of CO_2. Typical reaction conditions for the isopropylation of IBB were 3.9 g of IBB (25 mmol), 1.5 g of 2-propanol (25 mmol), and 0.125 g of the catalyst, with 8–12 MPa CO_2 pressure at 130–170 °C for 12 h. Dry ice, an amount calculated for target pressure, was placed with IBB, 2-propanol, and the catalyst in an autoclave before heating. After reaching the reaction temperature, the reaction was started by the agitation, and the pressure and the temperature were kept constant throughout the reaction. The pressures at reaction temperatures were almost the same as target pressures by calculating from the weight of dry ice. After the reaction, the reactor was depressurized very slowly after cooling in an ice bath. The contents of the reactor were extracted with

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Table 1. Isopropylation of IBB over Typical Zeolite Catalysts[a)]

Catalysts	Conv. /mol %	Selectivity/mol %				4-/3-IBC
		2-IBC	3-IBC	4-IBC	DIPIBB	
MOR(26)	18.5	—	22.9	77.1	—	3.4
BEA(26)	40.8	14.5	40.7	20.8	4.2	0.51
FAU(30)	40.0	11.7	13.0	31.8	34.3	2.4
MFI(54)	—	—	—	—	—	—
MEL(49)	—	—	—	—	—	—

a) Reaction conditions: IBB, 3.35 g (25 mmol); 2-propanol, 1.50 g (25 mmol); catalyst, 0.50 g; CO_2 pressure, 11 MPa; temperature, 150 °C; period, 12 h.

acetone and analyzed with a Shimadzu GC-14C or GC-18A gas chromatograph equipped with an Ultra-1 capillary column (25 m × 0.2 mm; film thickness: 0.33 µm; Agilent Technologies) for the products from IBB and BP, and with a TC-17 column (25 m × 0.25 mm; film thickness: 0.25 µm; GL Sciences, Tokyo) for the products from NP. The products were also confirmed by GC-MS (Shimadzu GC-MS5000). Thermogravimetric analyses (TGA) were conducted on a Shimadzu DTG-50 analyzer with a temperature-programmed rate of 10 °C min^{-1} in an air stream, where the catalyst used for the reaction was separated by filtration and dried overnight at 40 °C.

Results and Discussion

The Isopropylation of Isobutylbenzene (IBB). Table 1 shows the isopropylation of IBB over typical zeolites at 150 °C under 11 MPa of CO_2 pressure. 2-Propanol was used as the precursor of alkylating agents because it converted to propene under the reaction conditions. MOR(26), which has 12-membered ring (12-MR) pore entrances, gave a high selectivity for isobutylcumene (4-IBC) (77.1%), although IBB conversion was only 18.5%. There were no 2-IBC and diisopropylisobutylbenzene (DIPIBB) isomers formed. Here, CO_2 pressure was adjusted by the amount of dry ice, where the pressure was the same as calculated. We believe the water adhered to the dry ice and formed by the dehydration did not much influenced the catalysis judging from our previous results.[18–20]

High selectivity for 4-IBC was not achieved over BEA(26) and FAU(30) zeolites with three-dimensional 12-MR pore entrances, although moderate IBB conversion was recorded (≈40%). MFI(54) and MEL(49), which have smaller 10-MR pore entrances, showed no catalytic activity. These selectivity patterns were in accordance with the pore diameter and dimensionality of these zeolites and implied low shape selectivity for BEA and FAU zeolites. MFI and MEL have smaller pore diameters for the isopropylation of IBB.

Figure 1 summarizes the influence of the SiO_2/Al_2O_3 ratio of MOR on the isopropylation of IBB at 150 °C under 11 MPa of CO_2 pressure. The catalytic activity increased rapidly with increases in the SiO_2/Al_2O_3 ratio, and the selectivity for 4-IBC also improved slightly with the dealumination. In addition, MOR(110) showed a remarkable increase in IBB conversion (≈70%), along with a very high selectivity for 4-IBC (≈81%). However, further dealumination resulted in decreased catalytic activity with slight improvement in the selectivity for 4-IBC. These changes in the selectivity patterns of IBCs resulted in an overall increase of the 4-IBC/3-IBC ratio, which is the index of preferred recognition of 4- and 3-IBC by zeolites.

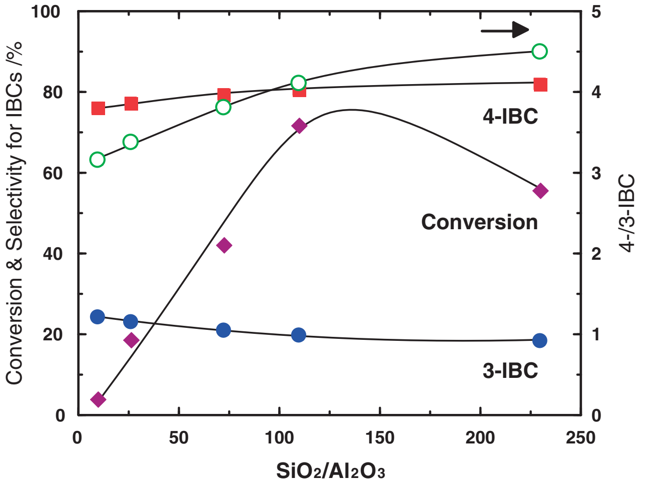

Figure 1. Influence of SiO_2/Al_2O_3 ratio of MOR on the isopropylation of IBB. Reaction conditions: IBB, 3.35 g (25 mmol); 2-propanol, 1.50 g (25 mmol); catalyst, MOR (SiO_2/Al_2O_3 = 9–230) 0.50 g; CO_2 pressure, 11 MPa; temperature, 150 °C; period, 12 h.

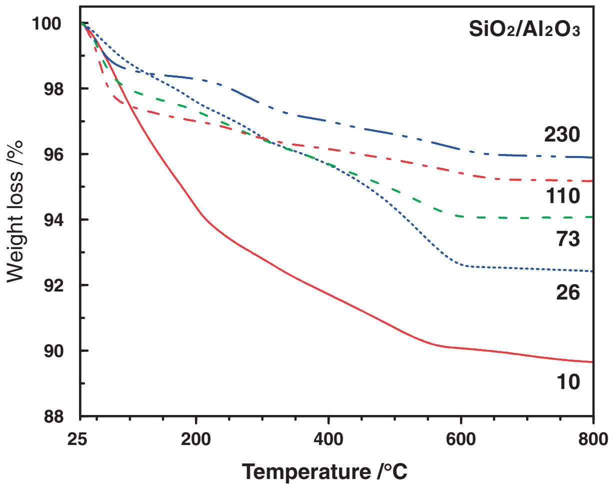

Figure 2. Influence of SiO_2/Al_2O_3 ratio of MOR on the TG profiles of the catalysts after the isopropylation of IBB. The catalysts were recovered by filtration and dried at 40 °C overnight.

Figure 2 shows the TGA profiles of the MOR catalysts after the reaction. The weight losses were strongly dependent on the SiO_2/Al_2O_3 ratio. In particular, the weight losses between 350–650 °C, which were due to coke formation during the reaction, decreased rapidly with increased ratios. SiO_2/Al_2O_3 ratios of 10, 26, 73, 110, and 230 resulted in weight losses of 2.2, 3.5, 2.0, 1.0, and 1.2%, respectively. These results signified that decreased coke formation enhanced catalytic activity although the dealumination decreased the number of acidic sites on MOR. Therefore, a reduced number of catalytic sites is not always the main reason for decreased catalytic activity. In retrospect, the reduction in coke formation in zeolite was more important for stable and improved catalytic perform-

Table 2. Influences of SiO_2/Al_2O_3 Ratio of FAU and BEA Zeolites on the Isopropylation of IBB[a)]

Catalysts	Conv. /mol %	Selectivity/mol %				4-/3-IBC
		2-IBC	3-IBC	4-IBC	DIPIBB	
BEA(26)	40.8	14.5	40.7	20.8	4.2	0.51
BEA(100)	9.7	7.3	40.0	52.7	—	1.3
FAU(30)	40.0	11.7	13.0	31.8	34.3	2.4
FAU(80)	2.4	28.7	25.8	45.5	—	1.8

a) Reaction conditions: IBB, 3.35 g (25 mmol); 2-propanol, 1.50 g (25 mmol); catalyst, 0.50 g; CO_2 pressure, 11 MPa; temperature, 150 °C; period, 12 h.

ance because deposited coke chokes pores and channels, and retard the catalysis.[30] However, deep dealumination of MOR to 230 of SiO_2/Al_2O_3 ratio decreased IBB conversion, suggesting that catalytic activity declined due to lower acid density even with the decrease in choking pores and channels. It must be noted that coke formation in *sc*-CO_2 medium was much lower than in conventional solvent-free or organic solvent.

Similar influences of the SiO_2/Al_2O_3 ratio of MOR were observed in liquid-phase isopropylation of NP and BP.[31,32] In both cases, the catalytic performances were enhanced by deep dealumination, with the highest catalytic activity and selectivity for 2,6-diisopropylnaphthalene (2,6-DIPN) and 4,4′-diisopropylbiphenyl (4,4′-DIPB) observed over MOR with a SiO_2/Al_2O_3 ratio of around 200.[4–6,31,32] These differences among IBB, NP, and BP were due to differences in reaction atmosphere (see below and our previous results[18–20]) and to the coke formation from them and their products. It was also noted that IBB could more easily diffuse through MOR channels than BP and NP, resulting in decreased catalytic performance in MOR with deep dealumination.

Table 2 summarizes the influences of SiO_2/Al_2O_3 ratio of BEA and FAU in the isopropylation of IBB. The catalytic activities decreased with increasing the SiO_2/Al_2O_3 ratios of BEA and FAU, particularly for FAU. The formation of DIPIBB was not observed over BEA and FAU with the high ratio. However, the formation of IBCs also decreased; however, the selective formation of 4-IBC was not observed because of the simultaneous formation of 2- and 3-IBCs.

The coke formation also decreased with increasing SiO_2/Al_2O_3 ratio of BEA and FAU (data not shown). These results are also quite different from the results of MOR. The decreases in catalytic activities of FAU and BEA by the increase in SiO_2/Al_2O_3 ratio are ascribed to the decrease in acid sites although these zeolites are not easily deactivated by the coke formation in them because of their three-dimensional pore system. However, the pores of one-dimensional zeolites like MOR were prone to the deactivation due to coke formation. These results indicate that the decrease in coke formation does not always result in improved catalytic performance of the zeolites. These differences were principally due to the pore structures of the zeolites, MOR, BEA, and FAU.

The existence of dense and strongly acidic sites on the zeolites also triggered the formation of 2-IBC, DIPIBB, and other products in a higher proportion. Furthermore, dense acid sites in aluminum-rich catalysts caused coke formation in higher amounts on the catalysts.[10,12,30] Clearly, higher amounts of coke formed on the catalysts during the isopropylation reduced the catalytic activity, but its effect was most significant in the case of one-dimensional MOR. Based on the above discussions, MOR(110) was selected for further studies.

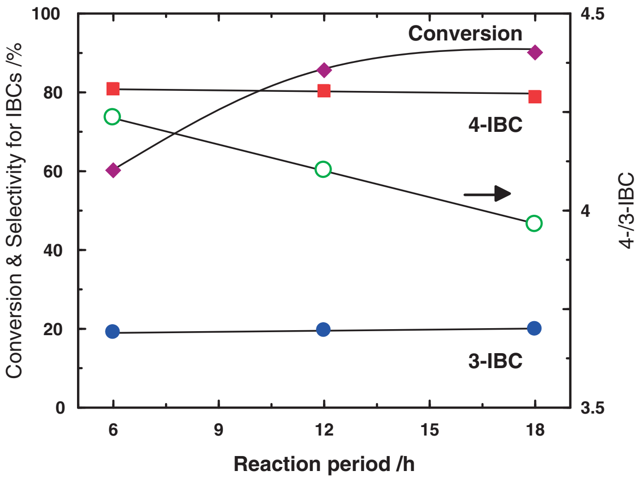

Figure 3. Influence of reaction time on the isopropylation of IBB over MOR(110). Reaction conditions: IBB, 3.35 g (25 mmol); 2-propanol, 1.50 g (25 mmol); catalyst: MOR(110), 0.50 g; CO_2 pressure, 11 MPa; temperature, 150 °C; period, 6, 12, and 18 h. Legends: see Figure 1.

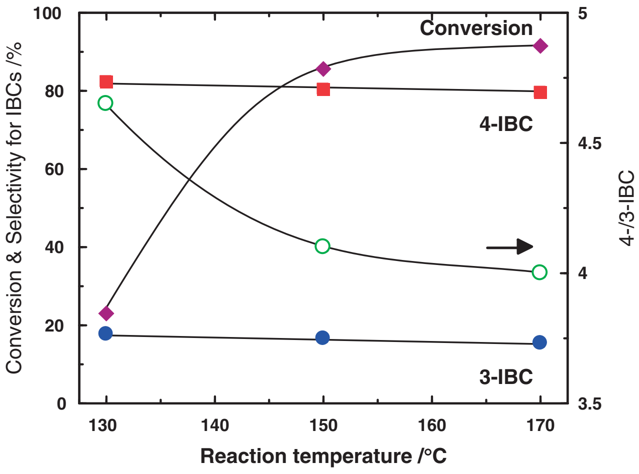

Figure 4. Influence of reaction temperature on the isopropylation of IBB over MOR. Reaction conditions: IBB, 3.35 g (25 mmol); 2-propanol, 1.50 g (25 mmol); catalyst: MOR(110), 0.50 g; CO_2 pressure, 11 MPa; temperature, 130–170 °C; period, 12 h. Legends: see Figure 1.

Figure 3 shows the influence of reaction time on the isopropylation of IBB at 150 °C over MOR(110). The IBB conversion increased with reaction time under *sc*-CO_2 medium, however, the selectivity for 4-IBC decreased slightly with reaction time. Thus, the ratio of 4-/3-IBC gradually decreased from 4.2 to 4.0, although 2-IBC was not detected even after 18 h. The continuation of the reaction resulted in saturation of the IBB conversion, but prolonged reaction times also triggered the formation of a small amount of DIPIBB (1.2%). Thus, it is obvious that external acid sites catalyzed the formation of 3-IBC and DIPIBB isomers.

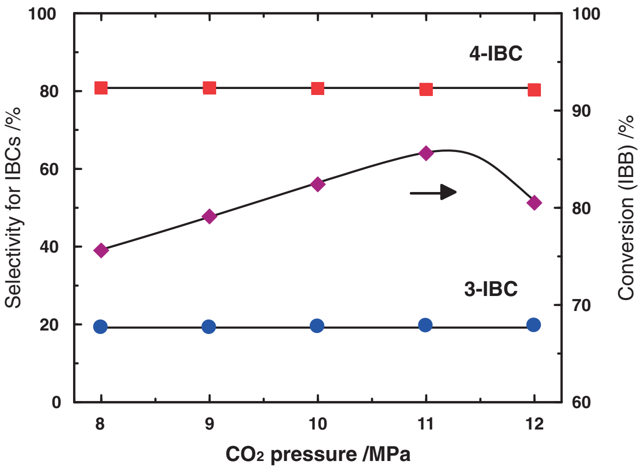

Figure 5. Influence of CO$_2$ pressure on the isopropylation of IBB over MOR(110). Reaction conditions: IBB, 3.35 g (25 mmol); 2-propanol, 1.50 g (25 mmol); catalyst: MOR(110), 0.50 g; temperature: 150 °C; CO$_2$ pressure, 8–12 MPa; period, 12 h. Legends: see Figure 1.

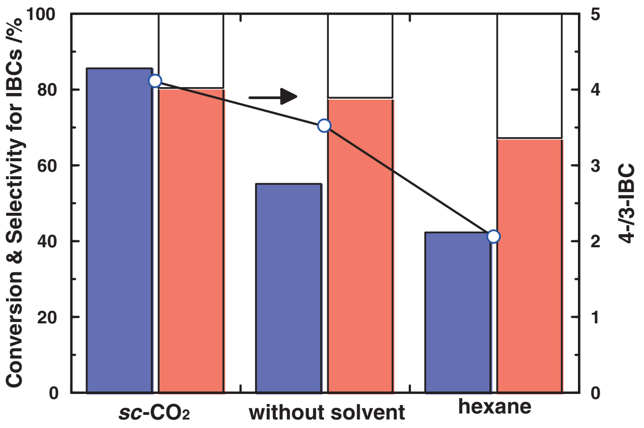

Figure 6. Isopropylation of IBB over MOR(110) in different reaction media. Reaction conditions: IBB, 3.35 g (25 mmol); 2-propanol, 1.50 g (25 mmol); catalyst: MOR(110), 0.50 g; CO$_2$ pressure, 11 MPa; temperature, 150 °C; period, 12 h or as stated in the footnote. A conventional reaction was carried out in hexane under autogeneous pressure. The reaction without solvent was carried out at 11 MPa of N$_2$ pressure. Legends: 🟦: Conversion; 🟥: 4-IBC; □: 3-IBC; ○: 4-/3-IBC.

Figure 4 shows the influence of reaction temperature on the isopropylation of IBB under 11 MPa of CO$_2$ pressure over MOR(110). As expected, IBB conversion increased with temperature, while the selectivity for 4-IBC gradually decreased from 82.3% at 130 °C to 79.6% at 170 °C. On the contrary, the formation of 3-IBC and DIPIBB (0.5% at 170 °C) increased slightly with temperature, accompanying a decrease in 4-/3-IBC ratio. Nevertheless, 2-IBC was not formed even at 170 °C.

Figure 5 shows the influence of CO$_2$ pressure on the isopropylation of IBB at 150 °C over MOR(110). The IBB conversion increased almost linearly up to 11 MPa of CO$_2$ pressure. However, further increases in CO$_2$ pressure slightly decreased the IBB conversion due to higher CO$_2$ density. The higher CO$_2$ pressures may decrease the access of the reactant molecules to the catalytic sites because of filling the channels with highly dense CO$_2$ in.[13–15] It is important, however, to note that the selectivity for 4-IBC, represented as the 4-/3-IBC ratio, remained almost constant with varied CO$_2$ pressure. Nevertheless, higher CO$_2$ concentrations reduced coke formation on the catalysts, which likely allowed the formation of 3-IBC in a slightly higher fraction.

Figure 6 shows the influence of reaction atmosphere of the isopropylation of IBB at 150 °C over MOR(110). The reaction performed in *sc*-CO$_2$ medium showed very high conversion (≈80%) as well as high selectivity for 4-IBC (80%). On the other hand, conventional liquid-phase reaction under autogeneous pressure in hexane (used as solvent) showed lower conversions. The conversion of the isopropylation without solvent by using neat substrate under 11 MPa of N$_2$ pressure was lower conversion than that in *sc*-CO$_2$ medium, but higher than that in hexane. In addition, the selectivity for 4-IBC in hexane was much less (≈67%) than that in *sc*-CO$_2$ medium. However, the selectivity without solvent was almost the same as under the *sc*-CO$_2$ atmosphere. In all cases, there was no formation of 2-IBC, and only small amounts of DIPIBB isomers (1.0–1.2%) were identified in the product mixture. These results indicate that *sc*-CO$_2$ was an excellent reaction medium for the isopropylation of IBB. As expected, the reaction carried out with neat reactants under autogeneous pressure also produced similar results to that observed under 11 MPa of N$_2$ pressure, indicating that the inert N$_2$ gas had no significant influences on the promotion of the isopropylation of IBB. The faster diffusion of reactants/products and efficient removal of coke precursors from the zeolitic channels promoted by *sc*-CO$_2$ medium is responsible for the higher IBB conversion and higher selectivity for 4-IBC in comparison with those in conventional reaction systems in hexane solvent or without solvent.

Coke formation over acid sites is considered one of the principal reasons for rapid deactivation of the catalysts. Enhanced catalyst performances in *sc*-CO$_2$ medium were thus achieved due to lower coke formation. This was visually observed based on the different colors of the catalysts used: off-white in the *sc*-CO$_2$ medium, and dark yellow in hexane and without solvent under N$_2$ pressure. In addition, TGA profiles of the used catalysts revealed that soft coke (≈1 wt %; weight loss in the range of 350–650 °C) was predominantly found in the catalyst used under *sc*-CO$_2$ medium as shown in Figure 7. However, after the reactions in hexane and without solvent, the catalysts contained much higher amounts of coke: 10 wt % in hexane and 12–14 wt % without solvent. Thus, the coke in *sc*-CO$_2$ formed was much less than those in hexane and without solvent. These results unambiguously demonstrated the superiority of *sc*-CO$_2$ medium for chemical transformations that are prone to the decrease in coke formation. Similar decreases in coke formation in *sc*-CO$_2$ medium were also found in the *tert*-butylation of phenol[18] and *p*-cresol.[19]

Table 3 shows the recycle and regeneration of MOR(110) in the isopropylation of IBB. The results showed the highest selectivity for 4-IBC. Nevertheless, the IBB conversion over MOR(110) reused after filtration and subsequent drying dropped considerably during the 1st run. In fact, the coke

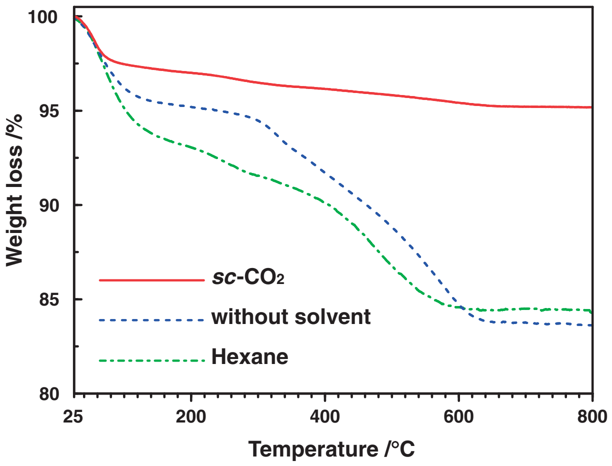

Figure 7. Influence of reaction media on the TG profiles of the catalysts after isopropylation of IBB. Reaction conditions: see Figure 6. The catalysts were recovered by filtration and dried at 40 °C overnight.

Table 3. Recycle and Regeneration of MOR Used in the Isopropylation of IBB[a)]

Catalysts	Conv. /mol %	Selectivity/mol %				4-/3-IBC
		2-IBC	3-IBC	4-IBC	DIPIBB	
MOR(110)	85.6	—	19.6	80.4	—	4.1
MOR(110)[b)]	47.3	—	17.8	82.2	—	4.6
MOR(110)[c)]	79.7	—	19.4	80.6	—	4.2

a) Reaction conditions: IBB, 3.35 g (25 mmol); 2-propanol, 1.50 g (25 mmol); catalyst: MOR(110), 0.50 g; CO_2 pressure, 11 MPa; temperature, 150 °C; period, 12 h. b) Second run for MOR(110) after filtration and drying of the catalyst. c) After calcination of MOR(110) used for second run.

could cover the active sites, and reduce the channel size, resulting in decrease in catalytic activity and increase in the selectivity for 4-IBC. Regeneration of MOR(110) used for a 2nd run by calcination at 500 °C confirmed that the catalysts retained activity and similar product selectivity with respect to the fresh catalyst.

Isopropylation of Naphthalene (NP). The isopropylation of NP with 2-propanol over MOR(128) in *sc*-CO_2 medium yielded isopropylnaphthalene (IPN) and diisopropylnaphthalene (DIPN) isomers (Figure S1 in Supporting Information). Yields of these alkylates increased with the increases in reaction temperature. The formation of alkylates occurred with the aid of *sc*-CO_2 medium. The *sc*-CO_2 medium enhanced the diffusion of NP and its products in and out of the MOR channels because of the high solubility of organic compounds in it, resulting in efficient catalysis even at low amounts of alkylating agent in our work.

Figure 8 shows the influences of reaction temperature on the isopropylation of NP over MOR(128) in *sc*-CO_2 medium. The selectivity for β,β-DIPN (2,6- and 2,7-DIPN) was around 90% at all temperatures because β,β-DIPN was the least bulky among the possible isomers. The selectivity for β,β-DIPN remained almost constant over the range of 140–170 °C. These results meant that the less bulky β,β-DIPN predominated over the other bulky isomers, and 2,6-DIPN favored over 2,7-DIPN in the β,β-DIPN isomers. This difference was caused by steric interaction with the MOR channels in the transition states because 2,6-DIPN had less steric hindrance than 2,7-DIPN in the MOR channels.[4–6]

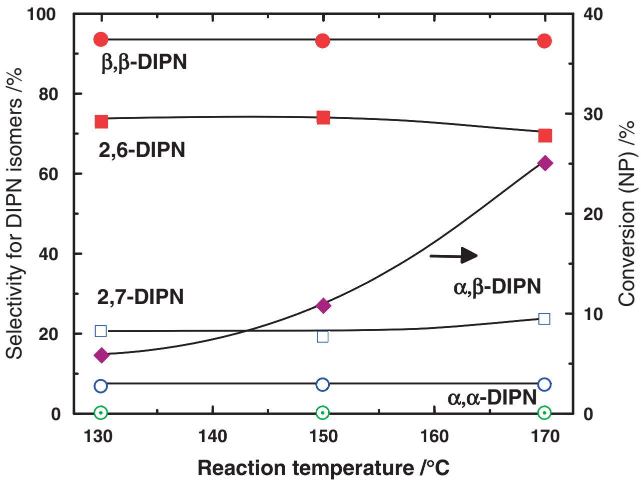

Figure 8. Influence of reaction temperature on the isopropylation of NP over MOR(128). Reaction conditions: NP, 6.25 mmol (800 mg); 2-propanol, 6.25 mmol (1.11 g); catalyst: MOR(128), 125 mg; temperature, 130–170 °C; period, 12 h; CO_2 pressure, 11 MPa.

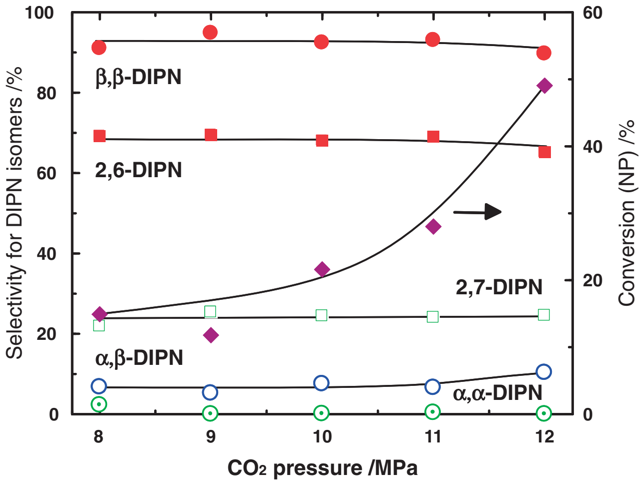

Figure 9. Influence of CO_2 pressure on the isopropylation of NP over MOR(128). Reaction conditions: BP, 6.25 mmol (800 mg); 2-propanol, 6.25 mmol (1.11 g); catalyst: MOR(128), 125 mg; temperature, 150 °C; period, 12 h; CO_2 pressure, 8–12 MPa.

There was no significant decrease in the selectivities for β,β- and 2,6-DIPN observed from increasing the reaction temperature in the isopropylation of NP in *sc*-CO_2 medium. This observation was due to lower reaction temperature, which prevented the isomerization of 2,6-DIPN at external acid sites compared to the results in conventional conditions.

The influences of CO_2 pressure on the yields of IPN and DIPN isomers are summarized in Figure S2 in Supporting Information. The catalytic activity increased with increasing CO_2 pressure, resulting in increased yields of IPN and DIPN isomers.

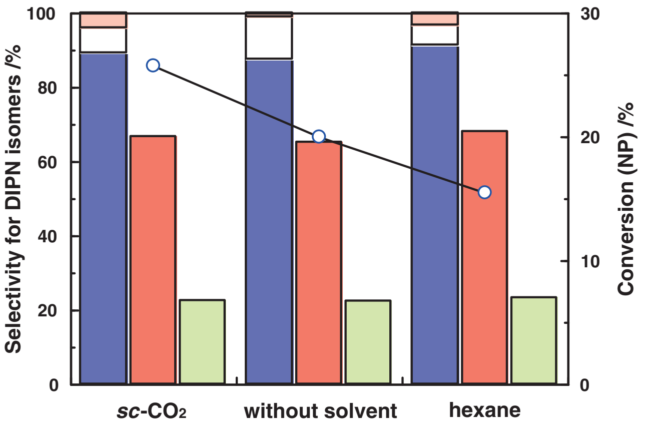

Figure 10. Isopropylation of NP over MOR(128) in different reaction media. Reaction conditions: NP, 6.25 mmol (800 mg); 2-propanol, 6.25 mmol (1.11 g); catalyst: MOR(128), 125 mg; temperature, 130–170 °C; period, 12 h; CO_2 pressure, 11 MPa. A conventional reaction was carried out in hexane under autogeneous pressure. The reaction without solvent was carried out at 11 MPa of N_2 pressure. Legends: 🟦: β,β-DIPN, □: α,β-DIPN; 🟧: α,α-DIPN; 🟥: 2,6-DIPN; 🟩: 2,7-DIPN; ○: Conversion.

Figure 9 shows the influences of CO_2 pressure on the selectivities for DIPN isomers in the isopropylation of NP over MOR(128) in sc-CO_2 medium. Apparently, there was no significant change in the selectivities for β,β- and 2,6-DIPN in spite of the increased catalytic activity with increased CO_2 pressure. Because increased CO_2 pressure enhanced the solubility of organic compounds, NP, its alkylated products, and propene, could easily diffuse in and out of MOR channels in dense sc-CO_2, which resulted in enhanced catalytic activity. However, the higher diffusivity of NP and its products under increased CO_2 pressure did not influence product selectivity. These observations indicate that isopropylation occurred in the MOR channels and that the bulky transition states were excluded by the channels, resulting in the preferential formation of the less bulky β,β- and 2,6-DIPN isomers. Furthermore, the differences between NP and IBB observed in this study are due to the difference in solubility of both compounds, because solubility of nonpolar organic compounds in nonpolar sc-CO_2 medium are generally related to molecular weight of the compounds.[13,33] IBB is more easily dissolved in the sc-CO_2 medium even at lower CO_2 pressure in comparison with NP and BP. These indicate that the isopropylation of IBB was less affected by CO_2 pressure than that those of NP and BP.

Figure 10 shows the isopropylation of NP over MOR(128) in different reaction media. sc-CO_2 medium showed higher NP conversion than other conventional reaction media. However, there was no difference in the selectivity for β,β- and 2,6-DIPN. It was envisaged that the higher activities were due to rapid removal of coke precursors, such as alkylated NP and propene oligomers from catalytic sites.

Isopropylation of Biphenyl (BP). The isopropylation of BP with 2-propanol over MOR(128) in sc-CO_2 medium yielded isopropylbiphenyl (IPBP) and diisopropylbiphenyl (DIPB) isomers, as shown in Figure S3 in Supporting Information. The yields of IPBP and DIPB increased with increasing reaction temperature, as also observed in the isopropylation of NP. The formation of alkylates was also enhanced with the use of sc-CO_2 medium. Thus, the diffusion of BP and its products in and out of the channels was enhanced by sc-CO_2 medium, resulting in efficient catalysis even at lower amounts of alkylating agent.

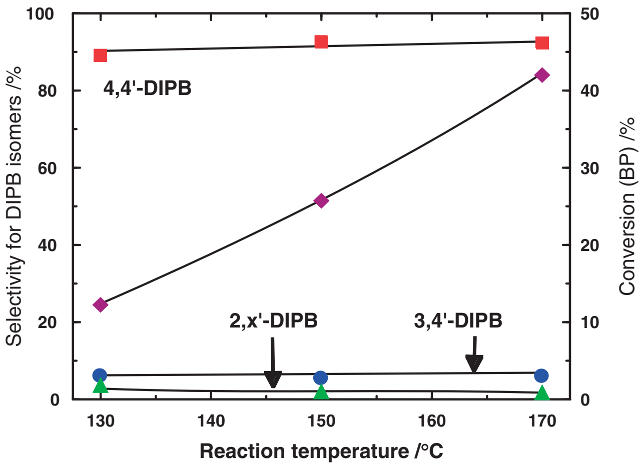

Figure 11. Influence of reaction temperature on the isopropylation of BP over MOR(128). Reaction conditions: BP, 6.25 mmol (964 mg); 2-propanol, 6.25 mmol (1.11 g); catalyst: MOR(128), 125 mg; temperature, 130–170 °C; period, 12 h; CO_2 pressure, 11 MPa.

Figure 11 summarizes the influence of reaction temperature on the isopropylation of BP over MOR(128) in sc-CO_2 medium. 4,4′-DIPB was preferentially obtained with a selectivity around 90% in the range of 130–170 °C. These results suggested that the increase in reaction temperature also enhanced the reaction in sc-CO_2 medium, and that the shape-selective formation of 4,4′-DIPB occurred inside the MOR channels through a restricted transition state mechanism.[4,6,32]

Increased CO_2 pressure also increased the formation of IPBP and DIPB in the isopropylation of BP over MOR(128) for the same reasons discussed for NP (Figure S4 in Supporting Information). These results also indicate sc-CO_2 enhanced the alkylation of BP because increased solubility of BP and its products accelerate the access to the acid sites in the MOR channels.

Figure 12 summarizes the influence of the CO pressure on the selectivity for DIPB isomers in the isopropylation of BP over MOR(128) in sc-CO_2 medium. Increased CO_2 pressure remarkably enhanced the formation of 4,4′-DIPB, and the selectivity for 4,4′-DIPB was as high as 90% even under increased CO_2 pressures. These results indicate that the formation of 4,4′-DIPB occurred inside the channels by a restricted transition state mechanism because the diffusion of BP and its products into the channels was enhanced by increased pressure.

sc-CO_2 Medium for the Alkylation of Aromatic Hydrocarbons. Coke is inevitably formed during acid catalysis over solid acid catalysts under liquid and vapor phase conditions. Coke forms on acidic sites, and causes the deactivation of catalytic sites. Coke formed in zeolite chokes their channels and pores, resulting in significant reductions in catalytic performance. For these reasons, the prevention of coke

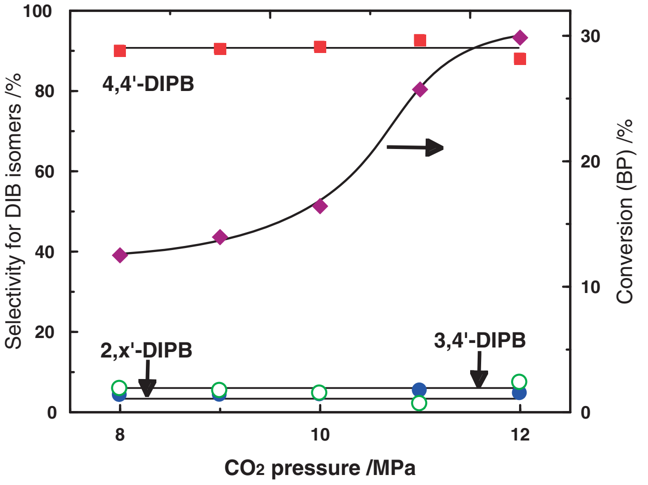

Figure 12. Influence of CO_2 pressure on the isopropylation of BP over MOR(128). Reaction conditions: BP, 6.25 mmol (964 mg); 2-propanol, 6.25 mmol (1.11 g); catalyst: MOR(128), 125 mg; temperature, 150 °C; period, 12 h; CO_2 pressure, 8–12 MPa.

formation in zeolite catalysis is the most urgent issue for the establishment of green chemical processes.

Solid acid catalysis in *sc*-CO_2 medium is well known for the reduction of coke formation.[18–21] In particular, coke precursors, probably alkylated polynuclear aromatics formed from the reactants/products, can easily diffuse from active sites to the bulk phase because of high solubility in *sc*-CO_2 medium, resulting in easy removal of these precursors. Therefore, the active sites are not deactivated during catalysis, resulting in the significant reduction of coke formation. However, coke precursors in conventional reactions with or without organic solvent mostly remain at the acidic sites and hardly diffuse to bulk phase during the catalysis, preventing the cleaning of the catalytic surfaces. These properties of *sc*-CO_2 medium enhance catalysis at clean active sites.

As shown in Figure 7, coke formation in *sc*-CO_2 medium is much lower than in conventional systems using hexane as solvent or without solvent under N_2 atmosphere in the isopropylation of IBB over MOR(110). Thus, low coke formation in the *sc*-CO_2 medium could enhance the catalytic performance of MOR, resulting in high catalytic activities with highly selective formation of 4-IBC.

Catalytic activities were increased by increasing the CO_2 pressure in *sc*-CO_2 medium in the isopropylation of NP and BP (Figures 9 and 12). These phenomena were due to the maintenance of clean active sites by the diffusion of coke precursors. Moreover, the reactants and products more easily diffused in and out of MOR channels in *sc*-CO_2 medium because of their increased solubility with increasing pressure. Thus, the isopropylation of NP and BP occurred effectively in *sc*-CO_2 medium, resulting in high conversion and high selectivities for 2,6-DIPN and 4,4′-DIPB at relatively low temperatures (below 170 °C). The isopropylation reactions in this work were carried out by using limited amounts of alkylating agent. We can expect much higher conversion with high formation of 2,6-DIPN and 4,4′-DIPB in the presence of sufficient amounts of alkylating agent.

The results in this work demonstrated that *sc*-CO_2 medium is a potential system for the prevention of catalyst deactivation by severe coking and for improvement of activity in solid acid catalysis, resulting in the establishment of efficient green chemical catalysis with low environmental burden. Furthermore, the catalyses in *sc*-CO_2 medium can also get rid of huge quantities of organic solvent waste and simplify post-reaction separation processes.

Conclusion

Supercritical CO_2 (*sc*-CO_2) as reaction medium can remarkably enhance the catalytic activity and selectivity for 4-isobutylcumene (4-IBC) in the isopropylation of isobutylbenzene (IBB) over H-mordenite (MOR), particularly MOR(110) with high dealumination. Similarly, highly shape-selective formation of the least bulky isomers, 2,6-diisopropylnaphthalene (2,6-DIPN) and 4,4′-diisopropylbiphenyl (4,4′-DIPB) was observed in *sc*-CO_2 medium in the isopropylation of naphthalene (NP) and biphenyl (BP), respectively, over dealuminated MOR(128) at 140–170 °C and 14 MPa. *sc*-CO_2 medium renders active acid sites free from coke formation through faster diffusion of reactants and products in zeolite catalyst and also through efficient dissolution of coke precursors. Thus, deactivation of the catalyst is reduced substantially without losing shape-selectivity.

These results demonstrate that *sc*-CO_2 medium can prevent deactivation of catalyst by severe coking and improve the selectivity of the desired product(s). The results in this work represent a new path for green catalysis. Further investigations on these aspects are currently ongoing and will be reported in due course.

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Supporting Information

Figure S1: Influences of reaction temperature on the isopropylation of NP, Figure S2: Influences of CO_2 pressure on the isopropylation of NP, Figure S3: Influences of reaction temperature on the isopropylation of BP, and Figure S4: Influences of CO_2 pressure on the isopropylation of BP. These materials are available free of charge on the Web at http://www.csj.jp/journals/bcsj/.

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