## Shape-selective Synthesis of 2,6-Diisopropylnaphthalene over H-Mordenite Catalyst

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2,6-DiisopropyInaphthalene is selectively produced in the liquid phase alkylation of naphthalene with propene or propan-2-ol over H-mordenite catalyst.

2,6-Dialkylnaphthalenes are useful monomeric starting materials for the preparation of liquid crystal polymers. However, it is difficult to obtain 2,6-dialkylnaphthalenes selectively in the alkylation of naphthalene with conventional method such as Friedel-Crafts alkylation<sup>1,2</sup> and gas phase reaction over silica/alumina catalysts.<sup>3,4</sup> This is because naphthalene has eight hydrogen atoms, which can be easily substituted with alkyl groups and various reactions such as alkylation, isomerization and transalkylation occur at the same time under the conventional alkylation conditions. Accordingly, it is necessary to control the substitution positions of naphthalene and the reaction pathway. We tried to regulate them in the liquid-phase alkylation of naphthalene by using zeolite catalysts, which are well known as shape selective catalysts for alkylation of benzene derivatives<sup>5,6</sup> and found that the H-mordenite (HM) catalyst shows a selectivity for the formation of 2,6-diisopropylnaphthalene (2,6-DIPN) in the reaction of naphthalene with propene or propan-2-ol.

Table 1 Properties of catalysts

Cat.	Specific <sup>a</sup> surface area/m <sup>2</sup> g <sup>-1</sup>	Si : Al <sub>2</sub> ratio	Acid sites <sup>b</sup> / mmol g <sup>-1</sup>			
НМ	608	25.3	0.69			
HY	1034	7.3	0.96			
HL	546	6.1	0.49			
H-ZSM5	416	70	0.44			

<sup>*a*</sup> Obtained by the Brunauer–Emmett–Teller method. <sup>*b*</sup> Obtained by NH<sub>3</sub> temperature programmed description (TPD), catalysts were evacuated at 873 K for 1 h, exposed to NH<sub>3</sub> at 423 K for 1 h, and then evacuated at 423 K for 1 h. TPD measurement was done from 423 to 873 K with a heating ratio of 10 K min<sup>-1</sup> and with He as the carrier gas having a flow rate of 100 cm<sup>3</sup> min<sup>-1</sup>.

Table 2 Catalytic isopropylation of naphthalene with propene

Naphthalene (0.27 mol), propene or propan-2-ol (0.48 mol), the catalyst (7.0 g) and n-undecane (240 ml) were put in a 500 ml autoclave and stirred at 240 or 160 °C for 5–8 h. HM (TSZ-660HOA) and HL (TSZ-500HOA) are from TOSOH Co., Ltd., Tokyo. HY is from Catalysts & Chemicals Co., Ltd., Tokyo. H-ZSM5 was synthesized by the conventional method.<sup>7</sup> The properties of these catalysts are shown in Table 1. The reaction mixture was analysed by GLC with a 50 m capillary column of OV-17 at 180 °C. The products were separated by distillation, crystallization and preparative gas chromatography and confirmed by GC-MS with the above column, and <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy. Table 2 lists typical results in the isopropylation of naphthalene using propene as the isopropylating reagent.

First, the activities of the zeolites used here decrease in the order HY >HL > HM > H-ZSM5. In the reactions with HY and HL, which have relatively large pores, selectivity for the formation of 2,6-DIPN is not observed at 240 or 160 °C, or in the conventional methods. Furthermore, it can be seen from the time course at 240 °C that the yields of  $\alpha$ ,  $\alpha$ -isomers (1,4and 1,5-) and  $\alpha$ , $\beta$ -isomers (1,3-, 1,6- and 1,7-) decrease and those of  $\beta$ , $\beta$ -isomers (2,6-, 2,7-) increase as the conversion increases. This suggests that the isopropylation initially occurs at the  $\alpha$ -positions of naphthalene and then isopropyl substituents are rearranged to  $\beta$ -positions by isomerization, transalkylation and disproportionation, although the transalkylation and disproportionation with HY proceed much easier than those with HL. When the reaction temperature is lowered to 160 °C the rearrangement reactions are depressed, and the yields of  $\beta$ , $\beta$ -isomers are much lower than those of  $\alpha, \alpha$ - and  $\alpha, \beta$ -isomers. This is attributed to the  $\alpha$ -positions of naphthalene being more active and thermodynamically less stable than the  $\beta$ -positions, the channels of HY and HL being large enough for rearrangement of the isopropyl groups to occur. This is confirmed by the fact that 2,6-DIPN was converted to 1,6-DIPN in low yield below 160 °C and at a

Run	Cat. <sup>a</sup>	Temp./°C	Time/h	Conv. (%)	DIPN Yield (%)	Distribution of DIPN (%) <sup>bc</sup>						
						1,3	1,4	1,5	1,6	1,7	2,6	2,7
1 HY 2	HY	240	2	94.8	43.9	32.3	14.4	8.2	14.7	13.5	8.5	8.4
			8	96.1	47.7	23.7	0.6	0.2	6.8	4.9	32.6	31.2
		160	2	90.0	40.5	15.1	39.8	13.1	11.0	15.5	2.8	2.7
			8	94.8	45.4	20.0	36.0	12.7	11.6	13.0	3.3	3.4
3 HL 4	HL	240	2	92.2	42.5	23.1	32.1	10.0	11.2	16.2	3.8	3.4
			8	95.1	42.5	39.9	7.9	6.7	15.3	16.3	6.7	7.2
		160	2	66.6	23.5	14.4	38.0	12.4	10.1	18.6	2.9	2.7
			8	88.2	39.5	16.6	40.3	11.9	9.6	15.9	3.1	2.6
5	H-ZSM5	240	8	1.0	_	_						
6	HM	240	2	35.6	5.7	7.3	5.1	3.3	4.8	3.8	51.7	24.0
			8	68.3	18.4	5.3	3.8	1.9	7.1	6.1	50.8	24.9

<sup>a</sup> Pore size of catalysts:<sup>8</sup> HY, three dimensional channel of *ca*. 0.8 nm; HL, straight channel of *ca*. 0.8 nm; HM, straight channel of 0.67  $\times$  0.7 nm; H-ZSM5, three dimensional channel of 0.51 nm. <sup>b</sup> Molecular size of DIPN: (calculated by M/M and M/D method with POLYGRAF which is the molecular simulation software from Bio Design Co., Ltd., USA): 1,3-DIPN, 0.88  $\times$  1.04 nm; 1,4-DIPN, 0.73  $\times$  1.07 nm; 1,5-DIPN, 0.71  $\times$  1.16 nm; 1,6-DIPN, 0.71  $\times$  1.18 nm; 1.7-DIPN, 0.88  $\times$  1.10 nm; 2,6-DIPN, 0.65  $\times$  1.32 nm; 2,7-DIPN, 0.65  $\times$  1.25 nm. <sup>c</sup> Trace amounts of other isomers were produced.

higher temperature converted mainly to 2,7-DIPN in the transalkylation of 2,6-DIPN over HY catalyst. However, H-ZSM5, which should have enough acidity for the isopropylation to occur as it does with HY and HL, shows little activity. This is because the pores in H-ZSM5 are too small to allow the isopropylation of naphthalene to occur.

In the reaction with HM, the product distribution is completely different from those with the other catalysts; that is, the selectivities for formation of  $\beta$ , $\beta$ -isomers are much higher than those for the  $\alpha, \alpha$ - and  $\alpha, \beta$ -isomers and do not change with the time. Generally,  $\beta$ , $\beta$ -isomers of dialkylnaphthalene are smaller in molecuar size than  $\alpha, \alpha$ - and  $\alpha, \beta$ isomers. From the above result, the pores in HM are so small that propene or propan-2-ol cannot attack at the  $\alpha$ -positions of naphthalene. However, this size effect cannot account for the fact that about twice as much of the 2,6-isomer is formed than the 2,7-isomer, since they both seem to be of similar molecular size. Because of this, we deduce that the activated complex, which promotes the production of the 2,6-isomer, is formed more easily between naphthalene, propene and the wall of HM channels, for molecular models disclose that the 2,6isomer has a more linear structure than the 2,7-isomer. This means that the structure of the 2,6-isomer is more suited to move in the tight one-dimensional tunnels of HM compared with the 2,7-isomer. It is supported by the fact that the rate of the isopropylation with HM is not so fast and furthermore, the HM catalyst is able to adsorb the 2,6-isomer much more readily than the other diisopropylnaphthalene isomers.

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