Selective alkylation of naphthalene with *tert*-butyl alcohol over large pore zeolites

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HY zeolites exhibit high activity and selectivity for 2,6-di-(*tert*-butyl)naphthalene in the liquid phase alkylation of naphthalene with *tert*-butyl alcohol; moreover, the desired 2,6-isomer is easily separated from the reaction mixture by crystallization.

2,6-Dialkylnaphthalenes are valuable compounds for the preparation of polyester fibres and plastics with superior properties and of thermotropic liquid crystal polymers.[1,2] However, selective synthesis of 2,6-dialkylnaphthalenes by alkylation of naphthalene is difficult with conventional Friedel–Crafts catalysts[3] or solid silica–alumina catalysts[4] which lead to low β,β′-selectivities and equal amounts of the 2,6- and 2,7-isomers. Various zeolitic catalysts have been extensively studied for the alkylation of mononuclear aromatic hydrocarbons and proved to be the most promising solid acids for achieving highly shape-selective catalysis.[5] The use of the shape selective properties of zeolites in the alkylation of naphthalene is therefore thought helpful in the synthesis of 2,6-dialkylnaphthalenes, even though the average molecular dimensions of the two β,β′-isomers are very similar. Isopropylation of naphthalene has been investigated using different zeolite catalysts.[6–10] The formation of 2,6-diisopropylnaphthalene with a 2,6/2,7 ratio of 2–3 and a resultant low activity compared with large pore zeolites was observed over medium pore mordenite[6,7,9,10] zeolites. With the aim of achieving both high activity and 2,6-dialkylnaphthalene selectivity in the alkylation of naphthalene, the present work deals with the use of *tert*-butyl alcohol, which is more hindered than isopropanol, as the alkylating agent and large pore zeolites, such as HY and H-beta, as the catalysts. The two zeolites are different in the architecture of their pores (with supercages linked by 7.4 × 7.4 Å pores for Y and 7.6 × 6.4 Å and 5.5 × 5.5 Å interconnected channels for beta).

Table 1 Properties of zeolitic catalysts

Catalyst	Cationic form	Si/Al/mol	BET surface area/m^2 g^{-1}
HY(2.5)	NH_4	2.5	775
HY(6)	H	6	720
HY(20)	H	19.5	800
H-beta(12)	H	12.8	658
H-beta(25)	NH_4	25.8	718

Zeolite catalysts with varing Si/Al ratios (Table 1) were prepared by standard ion-exchange, calcination, steam dealumination and acid leaching procedures from two parent synthetic zeolites, faujasite (Si/Al = 2.5) and beta (Si/Al = 12.8). Activation of the H and NH_4 forms was achieved at 500 and 550 °C, respectively, for 6 h with a heating rate of 60 °C min^{-1} in a dry air flow. The reaction was carried out in a 0.16 l stirred autoclave reactor (Parr Instrument Company). For a typical run, 10 mmol of naphthalene, 20 mmol of Bu^tOH and 100 ml of cyclohexane as solvent were mixed together until uniform, and then freshly calcinated zeolite (0.5 g) was added. The reaction temperature was set at 160 °C. Samples were withdrawn periodically and analysed on a HP5890II gas chromatograph equipped with OV1 capillary column (25 m) and an FID detector. 2,6-Di(*tert*-butyl)naphthalene (DTBN) crystals with purity greater than 95% were obtained by recrystallization of the concentrated liquid products. GC–MS (HP5970) with the same column, together with ^1H and ^{13}C NMR spectroscopy, was used for the identification of products.

Typical reaction results are listed in Table 2. In all cases, 2-(*tert*-butyl)naphthalene (2-TBN) was the only monoalkylated product. This, plus the results of the isopropylation of naphthalene from the literature[6,7,9] and our previous study[8] (in which 1-isopropylnaphthalene is initially formed on HY zeolites), clearly shows that the shape-selective effect is in operation on the large pore zeolites, even for the monoalkylation reaction step when the more hindered *tert*-butyl alcohol is used as the alkylating reagent.

The activities of the different zeolites were in the order HY(20) > HY(6) > H-beta(25) > H-beta(12) ≫ HY(2.5). For 2,6-DTBN selectivity, which is defined as a percent of

Table 2 Reaction results of *tert*-butylation of naphthalene of different zeolites at 160 °C[a]

			Product distribution (mass%)			β,β′-selectivity for DTBN (%)[b]			
Catalyst	Reaction time/h	Naphthalene conv. (%)	2-TBN	DTBN	Others	2,6	2,7	2,6 + 2,7	2,6/2,7
HY(20)	2	52.4	44.1	53.1	2.7	83.8	14.1	97.9	5.9
	8	66.4	42.6	49.1	8.2	77.0	18.9	95.9	4.1
HY(6)	2	44.9	52.1	46.3	1.6	83.8	14.9	98.7	5.6
	8	54.0	46.1	49.9	4.1	81.0	18.0	99.0	4.5
HY(2.5)	2	~1.5							
H-beta(25)	2	32.6	90.0	9.0	1.0	52.2	47.8	100	1.1
	8	47.1	76.6	17.1	6.3	48.0	38.6	86.6	1.2
H-beta(12)	2	16.2	95.2	4.8	0	50.0	50.0	100	1.0
	8	42.0	85.2	13.2	1.6	53.0	47.0	100	1.1

[a] Reaction conditions: catalyst 0.50 g, naphthalene 10 mmol, *tert*-butyl alcohol 20 mmol, cyclohexane 100 ml, 2 MPa. [b] β,β′-DTBN with respect to total DTBN isomers.

Table 3 Reaction results of *tert*-butylation of naphthalene over HY(6) at different temperatures[a]

Temperature/°C	Reaction time/h	Naphthalene conv. (%)	Product distribution (mass%)			β,β′-selectivity for DTBN (%)[b]			
			2-TBN	DTBN	Others	2,6	2,7	2,6 + 2,7	2,6/2,7
160	2	44.9	52.1	46.3	1.6	83.8	14.9	98.7	5.6
	8	54.0	46.1	49.9	4.1	81.0	18.0	99.0	4.5
180	2	71.0	44.0	48.5	7.6	75.3	22.5	97.8	3.3
	8	81.9	47.1	40.1	12.9	52.1	38.4	90.5	1.4
200	2	70.8	52.3	33.3	14.4	42.0	46.2	88.2	0.9
	8	64.1	51.8	23.5	25.5	31.9	46.0	77.9	0.7

[a] Reaction conditions: catalyst 0.50 g, naphthalene 10 mmol, *tert*-butyl alcohol 20 mmol, cyclohexane 100 ml, 2 MPa. [b] β,β′-DTBN with respect to total DTBN isomers.

2,6-DTBN with respect to all DTBN isomers, the two HY zeolites HY(20) and HY(6) show a much higher selectivity than the two H-beta catalysts (*ca.* 80% for HY against *ca.* 50% for H-beta). Zeolites HY(20) and HY(6) exhibit almost the same product distribution, β,β′-selectivity, 2,6-DTBN/2,7-DTBN ratio and parallel changes with reaction time. Up to 83.8% 2,6-DTBN selectivity was obtained on HY(20) and HY(6) with a 2,6-DTBN/2,7-DTBN ratio of 5.6–5.9 and β,β′-selectivity (2,6 + 2,7) of 97.9–98.7% after 2 h at 160 °C. This is the first observation of such a high β,β′-selectivity and 2,6/2,7 ratio in the liquid phase alkylation of naphthalene. This could be logically attributed to the pore size effect of HY zeolite, which is capable of limiting the formation of isomers with relatively large dimensions. The 100% 2-TBN selectivity in the first reaction step could be another reason for such a β,β′-DTBN selectivity. Moreover, a 45–52% naphthalene conversion can be achieved after 2 h reaction at 160 °C over the two samples of HY(20) and HY(6), indicating interesting catalytic activity for such zeolites in the alkylation of naphthalene with *tert*-butyl alcohol. In contrast, HY(2.5) is almost inactive under the same reaction conditions (1.5% conversion after 2 h reaction). This can be accounted for by the inhibiting effect of large amounts of strongly adsorbed polar *tert*-butyl alcohol species in the pores of HY(2.5) zeolite due to its high density of acidic sites. In the reaction on H-beta zeolites, 2-TBN was observed as the main product (about 80 at 45% conversion) with relatively small amounts of DTBN derivatives. This may be attributed to the different architecture of their pores (absence of supercages), in which further alkylation of 2-TBN cannot occur or through which the dialkylated derivatives cannot freely move. The formation of DTBN on both H-beta zeolites with a 2,6-DTBN/2,7-DTBN ratio of *ca.* 1 may result from the alkylation reaction occurring on the external surface.

Detailed studies were thus focused on HY zeolites. As can be seen from Table 3, increasing the reaction temperature causes a dramatic decrease of the 2,6-DTBN selectivity and 2,6-DTBN/2,7-DTBN ratio (after 2 h reaction the 2,6-DTBN selectivities were 83.8, 75.3 and 42.0% at 160, 180 and 200 °C, respectively). These results indicate that secondary reactions take place more readily at high temperature, which would result in thermodynamic equilibrium products. When the reaction temperature is 160 °C, the rearrangement reactions are apparently depressed; only slight transformation from 2,6-DTBN to 2,7-DTBN occurred (2,6/2,7 ratio varies from 5.6 to 4.5 after 8 h reaction). At 200 °C, maximum conversion of naphthalene is obtained after *ca.* 2 h, but it is interesting to note a decrease of conversion with time, which indicates increasing amounts of naphthalene in the reaction mixture. This implies that secondary reactions, such as dealkylation, disproportionation or transalkylation of DTBN, can take place at this temperature, possibly on the external surface of the zeolite crystals. Some polybutene compounds, such as dimers and trimers of the *tert*-butyl group, were observed in the products, and the amount of these products increased remarkably with increasing temperature. *tert*-Butyl alcohol is consumed by these side reactions, so that it can be assumed that further alkylation reactions cannot occur, which may be another reason for the lower maximum conversion at 200 °C than at 180 °C.

The selective formation of 2,6-DTBN against 2,7-DTBN observed for HY zeolites could possibly arise from the difference in their diffusion kinetics. This has been recently demonstrated by Horsly *et al.*[11] using computational modelling of selective isopropylation of naphthalene over a medium pore mordenite zeolite. Even for different molecules with similar sizes, such as the 2,6- and 2,7-dialkylated naphthalene isomers,[6,12] there should be a difference in the interaction between molecule and zeolite pore, which may lead to a different diffusion rate. This may be the case for the selective formation of 2,6-DTBN on HY zeolites. Further studies are in progress to clarify this issue. The high ratio of 2,6-DTBN/2,7-DTBN observed in the present work should be helpful in understanding this new selective effect.

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