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Selective transalkylation of naphthalene and ethylnaphthalene over solid acid catalysts

Genki Takeuchi [1], Yasuhiro Shimoura and Tadanori Hara

Research and Development Laboratories, Nippon Steel Chemical Co., Ltd., Nakabaru, Sakinohama, Tobata-ku,
Kitakyushu-shi 804, Japan

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A high 2,6-diethylnaphthalene (2,6-DEN) isomer ratio (62%) and a good 2,6-DEN yield (46 mol%) were obtained by the transethylation of 2-ethylnaphthalene with tetraethylbenzenes over H-Y zeolite catalyst. Steric hindrance and electron density at the substitution sites of naphthalene are two influential factors for excellent selectivity. Silica–alumina catalyst, which cannot be expected to possess shape selectivity, also demonstrated a high 2,6-DEN selectivity.

Keywords: naphthalene; selective ethylation; 2,6-diethylnaphthalene; Y zeolite; transethylation

1. Introduction

2,6-dialkylnaphthalenes are key compounds leading to 2,6-naphthalenedicarboxylic acid (2,6-NDCA), a prospective monomer for preparation of high-performance polymers [1]. Selective preparation of 2,6-diisopropylnaphthalene (2,6-DIPN) has well been established over mordenite catalyst, a shape selective catalyst [2–4]. The corresponding ethylation over mordenite catalyst to produce 2,6-diethylnaphthalene (2,6-DEN), however, has not yet been reported, presumably because ethylated naphthalenes are smaller in size than the corresponding isopropylated ones. Other zeolites, which have a smaller pore size than the mordenite, were utilized, but the isomer selectivity and yields of 2,6-DEN were not satisfactory [5]. Though 2,6-DEN is a more preferable raw material for manufacturing 2,6-NDCA than 2,6-DIPN because of its high oxidation yield of 2,6-NDCA, selective synthesis of 2,6-DEN has not yet been achieved.

We here report on a highly selective synthesis of 2,6-DEN via transethylation of naphthalene over solid acid catalysts, which does not show shape selectivity. The work described in this paper was presented at the 28th Meeting of the Japan Aromatic Industry Association [6].

2. Experimental

Starting materials are naphthalene, 2-ethylnaphthalene (99.5% pure, Nippon Steel Chemical Co.), ethylene (Sumitomo Seika Co.), and diethyl-, triethyl-, and tetraethylbenzene (Nippon Steel Chemical Co.). Three types of solid acid catalysts, mordenite, Y zeolite (Toso Co.), and silica–alumina (Nikki Chemical Co.) were used. All of these H-type catalysts were calcined at 300°C for 18 h before use. Experiments were carried out batchwise in a 300 ml autoclave equipped with a magnetic stirrer and a

Table 1
Ethylation of naphthalene with ethylene [a]

Cat.	Reaction temp. (°C)	Reaction time (h)	Naph. conv. (%)	2,6-DEN yield (wt%)	DEN isomer composition (%)						2,6-DEN/ 2,7-DEN
					2,6-	2,7-	1,6-	1,7-	1,3-	other	
Si–Al_2	300	0.5	27.1	0.5	15.5	15.2	10.5	10.6	21.6	26.6	1.02
Si–Al_2	300	3.5	86.6	4.8	19.3	17.8	10.8	9.8	19.9	22.5	1.08
Si–Al_2	300	5.0	90.9	5.2	21.0	19.7	10.7	8.9	19.6	20.1	1.08
Y-Zeo.	270	4.0	85.1	5.0	17.8	15.8	11.1	10.9	19.8	24.6	1.12
Morde.	270	4.5	79.4	5.4	21.1	15.7	11.6	8.2	21.5	21.9	1.34
thermodynamic equilibrium (300°C)⟶					27	27	14	14	14	4	1

[a] Si–Al_2: silica–alumina, Y-Zeo.: H-Y zeolite, Morde.: H-mordenite. Naph.: naphthalene, DEN: diethylnaphthalene. DEN yield: DEN proportion in naphthalene and ethylated naphthalene. Cat./Naph = 0.2/1 (wt/wt). Reaction pressure was kept at 2 MPa during the ethylation.

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[1] To whom correspondence should be addressed.

Table 2
Transethylation of naphthalene with TeEBz over silica–alumina [a]

React. temp. (°C)	React. time (h)	Naph. conv. (%)	2,6-DEN yield (wt%)	DEN isomer composition (%) 2,6-	2,7-	1,6-	1,7-	1,3-	other	2,6-DEN/2,7-DEN
300	2	83.0	9.8	30.0	27.0	15.4	12.1	12.2	3.3	1.11
250	2	68.2	7.7	32.9	27.4	15.2	11.1	10.8	2.6	1.20
200	1	14.5	0.6	44.8	23.8	12.1	9.2	10.0	0.0	1.88
200	4	47.7	4.7	40.0	26.0	13.2	9.3	9.6	1.7	1.54
175	6	38.6	3.9	43.4	24.3	12.2	8.4	9.4	2.3	1.78
150	8	3.5	0.1	70.4	29.6	0.0	0.0	0.0	0.0	2.38

[a] Naph.: naphthalene, DEN: diethylnaphthalene, TeEBz: tetraethylbenzene. DEN yield: DEN proportion in naphthalene and ethylated naphthalene. TeEBz/reactant = 1.5 (wt/wt). Cat./(Naph + TeEBz) = 0.2/1 (wt/wt).

pressure gauge. Product analysis was performed by FID gas chromatography.

3. Results and discussion

3.1. Ethylation of naphthalene with ethylene

The results of the alkylation of naphthalene with ethylene in the presence of three types of catalysts at 270–300°C are summarized in table 1. As Fellmann pointed out [5], the 2,6-DEN isomer composition and the 2,6-DEN/2,7-DEN ratio are important indicators for selective ethylation of naphthalene. The selective ethylation requires the 2,6-DEN isomer composition to exceed the one at thermodynamic equilibrium and the 2,6-DEN/2,7-DEN ratio to exceed 1.0. Experimentally, we estimated the composition of DEN isomers at thermodynamic equilibrium, shown in table 1. All of the 2,6-DEN isomer compositions in table 1 were less than 27%, the value at thermodynamic equilibrium, and "other DENs", which have at least one ethyl group at the α-position, were formed in more than 20%. These results can be explained by the concept that the α-position of naphthalene, which has a higher π electron density than the β-position, is first ethylated, and the ethyl group introduced then migrates to the β-position to give products which are more thermodynamically stable [7]. Therefore, during the ethylation with ethylene, the value for the 2,6-DEN isomer composition would increase up to the one estimated at thermodynamic equilibrium. The 2,6-DEN/2,7-DEN ratio in table 1 remained to be 1.0–1.3 for these three catalysts. We concluded that selective ethylation of naphthalene with ethylene was impossible over the catalysts shown in table 1.

3.2. Transethylation of naphthalene with tetraethylbenzenes

The results of transethylation of naphthalene with tetraethylbenzenes over silica–alumina catalysts at 150–300°C are shown in table 2. In the transethylation which requires enough room for an activated complex at the transition state [8], α-ethylated DEN isomer formation was suppressed because of steric hindrance at the α-position of naphthalene. 2,6-DEN and 2,7-DEN, both of which have two ethyl groups in the β-positions, were main products among DEN isomers. Though the 2,6-DEN/2,7-DEN ratio was almost 1 at 300°C, the ratio increased with a decrease in reaction temperature and naphthalene conversion. At 150°C, the formation of DEN isomers, excluding 2,6-DEN and 2,7-DEN, was minimized and the 2,6-DEN/2,7-DEN ratio exceeded 2. Based on the experimental result at 150°C, we concluded that 2,6-DEN was formed selectively at the early stage of the transethylation.

We propose a possible mechanism of a high 2,6-DEN isomer composition in the reaction mixture during the transethylation as follows. The first ethyl group is introduced into the naphthalene nucleus, producing β(2)-ethylnaphthalene selectively because of steric hindrance at the α(1)-position. When the second ethyl group is introduced into the 2-ethylnaphthalene, the 6-position is ethylated selectively because of its higher HOMO π electron density (0.197 eV: calculated by MNDO method), compared with the 7-position

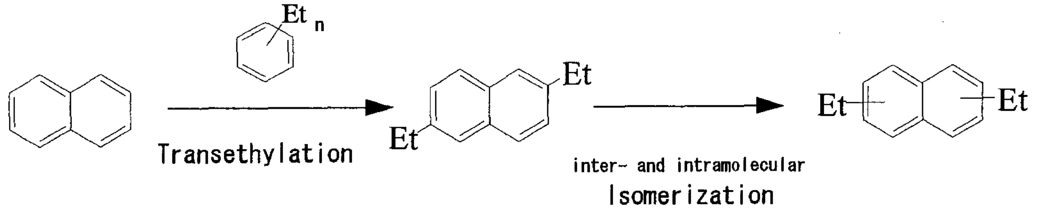

Fig. 1. Transethylation of naphthalene with polyethylbenzenes.

Table 3
Transethylation of naphthalene and 2-ethylnaphthalene (2-EN) with polyethylbenzenes over H-Y zeolite [a]

Ex. No.	Reactant	PEBz	Reaction temp. (°C)	Reaction time (h)	Naph. or 2-EN conv. (%)	DEN yield (wt%)	2,6-DEN yield (wt%)	DEN isomer composition (%)						2,6-DEN/ 2,7-DEN
								2,6-	2,7-	1,6-	1,7-	1,3-	other	
EX-1	Naph.	TeEBz	110	2	17.5	2.4	1.4	59.1	18.9	11.3	6.8	2.0	1.9	3.13
EX-2	Naph.	TeEBz	110	8	77.3	38.9	19.5	50.3	25.2	12.7	7.6	2.5	1.7	2.00
EX-3	Naph.	TeEBz	110	17	95.2	60.7	29.8	49.0	27.8	11.8	6.2	3.8	1.3	1.76
EX-4	2-EN	TeEBz	110	1	11.7	10.6	7.7	72.7	19.2	5.2	2.6	0.0	0.3	3.79
EX-5	2-EN	TeEBz	110	3	45.4	42.1	28.7	68.1	21.2	7.0	3.0	0.3	0.4	3.21
EX-6	2-EN	TeEBz	110	8	83.9	74.7	46.6	62.4	24.6	8.7	3.0	0.9	0.4	2.54
EX-7	2-EN	TrEBz	110	7	64.9	41.8	27.5	65.8	22.2	7.9	3.0	0.7	0.5	2.83
EX-8	2-EN	TrEBz	110	17	81.2	69.7	41.5	59.6	25.4	9.6	3.3	1.6	0.6	2.35
EX-9	2-EN	DEBz	110	8	22.9	15.3	8.3	54.3	29.7	9.0	4.7	1.2	1.1	1.83
EX-10	2-EN	DEBz	110	22	56.0	41.5	18.7	45.1	32.5	11.6	6.5	3.2	1.2	1.39

[a] PEBz: polyethylbenzene, DEBz: diethylbenzene, TrEBz: triethylbenzene, TeEBz: tetraethylbenzene. Naph: naphthalene, DEN: diethylnaphthalene. DEN yield: DEN proportion in naphthalene and ethylated naphthalene. PEBz/reactant = 4.0 (wt/wt). Cat./((Naph. or 2-EN) + PEBz) = 0.2/1 (wt/wt).

(0.083 eV: calculated by MNDO method). The transethylation into the 1-, 4-, 5-, 8- and 3-positions of 2-ethylnaphthalene was almost negligible because of the steric hindrance. As mentioned above, the transethylation of naphthalene produces 2,6-DEN in high selectivity, though this fact is not generally noticed, due to ready isomerization of 2,6-DEN to other DEN isomers (fig. 1). In case of the result at 150°C in table 2, the isomerization was suppressed due to low temperature.

We succeeded to adjust the reaction conditions to obtain a high yield of 2,6-DEN with maintaining its high selectivity. In order to suppress the isomerization of 2,6-DEN to other DEN isomers, lowering of reaction temperature is essential. For enhancement of the transethylation, we chose tetraethylbenzenes as transethylating agents and used them in a relatively large amount (fig. 1). For the reaction at low temperatures, H-Y zeolite is a more suitable catalyst than silica–alumina, because the acidity of the former is stronger than that of the latter.

As shown in table 3, a high isomer ratio and a high yield of 2,6-DEN were obtained at a low reaction temperature (110°C), using a large amount of TeEBz, in the presence of a stronger catalyst (H-Y zeolite). For example, the isomer ratio and yield of 2,6-DEN reached 50.3% and 19.5%, respectively, in the transethylation of naphthalene at 110°C for 8 h (Ex-2). The ratio of 2,6-DEN/2,7-DEN also reached 2.0. 2-ethylnaphthalene is a more readily available raw material for 2,6-DEN, because the isomer ratio and yield of 2,6-DEN reached 62.4 and 46.6%, respectively, at 110°C for 8 h (Ex-6).

Tetraethylbenzenes were the best transalkylating agent among di-, tri-, and tetraethylbenzenes in terms of the 2,6-DEN selectivity and DEN yield. For example, the DEN yield reached 42% for 3 h with tetraethylbenzenes (Ex-5). On the other hand, the reaction of 7 h (Ex-7) and 22 h (Ex-10) was necessary with tri- and diethylbenzenes to obtain the same DEN yield. Furthermore, the 2,6-DEN selectivities increased in the order of di-, tri-, and tetraethylbenzenes, that is, 45.1% with diethylbenzenes (Ex-10), 65.8% with triethylbenzenes (Ex-7), and 68.1% with tetraethylbenzenes (Ex-5). The highest selectivity of 2,6-DEN with tetraethylbenzenes is due to its remarkable capacity of transethylation to 2,6-DEN rather than isomerization to other DEN isomers (fig. 1).

We do not consider that this high 2,6-DEN selectivity is attributed to the shape selectivity of H-Y zeolite. Because silica–alumina catalyst, which cannot be expected to have shape selectivity, can also achieve a high 2,6-DEN selectivity, as shown in table 2.

4. Conclusion

Transethylation of naphthalene with tetraethylbenzenes over H-Y zeolite catalyst at comparatively lower temperatures minimizes product isomerization and gives high 2,6-DEN selectivity.

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