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Disproportionation of isopropylnaphthalene on zeolite catalysts

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Abstract

Disproportionation of isopropylnaphthalene (IPN) was tested over H-mordenite, HY, H-beta zeolites and over amorphous aluminosilicate in the range of 150–300 °C. High β, β-selectivity in diisopropylnaphthalene (DIPN) product obtained over zeolites was observed. However, the 2,6-DIPN/2,7-DIPN mole ratio was dependent on the pore structure of the applied zeolite and on the temperature. Over H-mordenites 2,6-DIPN was the most preferred isomer, whereas 2,7-DIPN was favored over HY and H-beta zeolites. Such disproportion in isomer predominating in the DIPN product can be explained by a bimolecular mechanism of disproportionation. Due to the zeolite pore architecture the bent transition-state complex, leading to 2,7-DIPN (HY and H-beta) or more linear, leading to 2,6-DIPN (H-mordenite), was preferred. At high temperatures the monomolecular disproportionation mechanism (dealkylation realkylation) dominated and concealed (simultaneously with side reactions) the shape-selectivity effect. As a result the 2,6-DIPN/2,7-DIPN mole ratio in the product approached equilibrium value.

Keywords: Shape selectivity; Zeolite; Disproportionation; Isopropylnaphthalene; Diisopropylnaphthalene

1. Introduction

2,6-Diisopropylnaphthalene (2,6-DIPN), isolated from the isomeric mixture, can be used as a raw material for the production of advanced polyester fibers, films, and plastics such as thermotropic liquid crystalline polymers [1,2]. Although the most abundant isomers in a DIPN mixture at thermodynamic equilibrium are 2,6- and 2,7-DIPN ($> 80\%$) [3–5], further improvement in 2,6-DIPN yield can be achieved if the synthesis is carried out over wide pore zeolites, such as mordenite, Y, beta, or L. Formation and diffusion of bulky DIPN isomers with substituents at α positions of the naphthalene nucleus are restricted in zeolite pores. Alkylation of naphthalene carried out over mordenite catalysts has an additional advantage; apart from high β, β-selectivity in diisopropylation, high 2,6-DIPN to 2,7-DIPN ratios can be observed [5–14].

The reasons of higher yield of 2,6-DIPN than 2,7-DIPN in the alkylation product are still widely discussed and they are not quite clear. Horsley et al. [8] proved with the help of molecular graphics and diffusion energy calculations that the more linear 2,6-DIPN molecule can migrate more easily than the 2,7-DIPN through the mordenite channels. The difference in diffusion between 2,6- and 2,7-DIPN was confirmed by DIPN sorption experiments [4,5]. According to some authors [6,11,15,16] a difference in the critical diameter between 2,6- and 2,7-DIPN molecules is too small to cause such differences. However, Tasi et al. [4] recently calculated the molecular dimensions of DIPN molecules and obtained a significantly smaller cross section of 2,6-DIPN than 2,7-DIPN.

Other authors [6,7,9] postulated that the activated complex producing 2,6-DIPN is less hindered in the mordenite pores than that for 2,7-DIPN. This supposition seems to be confirmed by Kim et al.'s [9] results who found high 2,6-DIPN/2,7-DIPN ratios both in the product encapsulated in the zeolite pores and in the bulk product outside the pores.

Song and co-workers [11,15] calculated frontier electron density for electrophilic substitution at different carbon atoms of the naphthalene nucleus and they found that for 2-isopropylnaphthalene (2-IPN) molecules position 6 is kinetically preferred to position 7. Therefore, the product formed in the spatially hindered environment in a mordenite channel is more abundant in 2,6-DIPN than 2,7-DIPN. However, this result is in contradiction with calculations of electrostatic potential for 2-IPN by Tasi et al. [4] who did not confirm distinguishing between positions 6 and 7 in electrophilic aromatic substitution.

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Regardless of the reason, shape-selectivity effects leading to high β-selectivity and high 2,6-DIPN/2,7-DIPN ratios can be affected by side reactions occurring on the external surface of zeolite and in the pore entrances. Alkylation of naphthalene molecules in the pore entrances can lead to high yields of 1,3-DIPN and 1,4-DIPN in the product [18]. Secondary side reactions such as disproportionation, transalkylation, and isomerization, occurring on the external surface of the zeolite crystals, can also play an important role in the synthesis of diisopropylnaphthalenes.

These side reactions can be suppressed by proper dealumination of catalyst or by deactivation of external active sites by deposition of compounds of silica, ceria, or other metal [9–11,13,19,20]. Although β-selectivity and 2,6-DIPN yield can be then improved, side reactions cannot be eliminated entirely. Moreover, secondary reactions, such as isomerization of 2,6- and 2,7-DIPN to one another [4] or disproportionation of 2-isopropylnaphthalene, are also possible in the pores.

The influence of side reactions, always accompanying alkylation, is frequently not considered. However, they cannot be neglected in the alkylation environment, especially when experiments are performed in a batch-type reactor and reaction time is in the range of several hours [5–14].

The aim of the present work was to test disproportionation of IPN over shape-selective catalysts applied in naphthalene alkylation and to verify the possible influence of the reaction on the alkylation product.

2. Experimental

Isopropylnaphthalene 99.7% pure (GC analysis) was isolated by distillation from alkylates obtained previously. Apart from 2-IPN (86.1% of total IPN) and 1-IPN it contained small amounts of isopropyltetralines, ethylnaphthalenes, and other alkylnaphthalenes with molecular masses of 184 and 198 (GC/MS).

Four zeolite catalysts in hydrogen form, HY, beta (HB), and two mordenites, high-silica (HM-1) and low-silica (HM-2), and amorphous aluminosilicate (AM) were tested in disproportionation of IPN. The SiO_2/Al_2O_3 mole ratios of the catalysts were 5.8, 25, 84, 9.9, and 13.4, respectively. More detailed characteristics of the catalysts, except for HM-2, are described elsewhere [18]. The hydrogen form of mordenite HM-2 (Na_2O content 0.32 wt%) was prepared from the Na form of Zeolon 900 (Norton Co.) by washing three times with ammonia chloride solution according to the standard procedure.

Disproportionation experiments were carried out in a fixed-bed reactor (5 g of catalyst) at 0.8 MPa. Before each experiment, the catalyst was activated at 450 °C in the flow of air for at least 2 h. Subsequently the air stream was replaced for nitrogen and temperature was lowered to the experimental temperature. Reactant mixture was recirculated through the catalyst bed at $F/W = 70\ g/(g_{cat}\ h)$. Such flow enabled the reactants to be one time passed through the catalyst bed every 6 min. Samples of products were analyzed by GC equipped with FID, using a 60-m-long HP-Innowax capillary column. Details of the analytical method and the DIPN isomers identification are described elsewhere [21]. To improve detection accuracy of DIPN isomeric composition, analyses of samples poor in DIPN were repeated using increased amounts of injected sample and integrating only the DIPN part of the GC spectra.

3. Results and discussion

Results of disproportionation experiments carried out over AM, HM-1, HM-2, HY, and HB catalysts are shown in Tables 1–5, respectively. Results such as the IPN conversion level, the 2-IPN content in monoisopropylnaphthalene (indicating isomerization of IPN), the DIPN content in the recirculated mixture (indicating disproportionation progress), and the isomeric composition of diisopropylnaphthalenes

Table 1
Results of IPN disproportionation over the AM catalyst

Temperature	Time	IPN conversion	2-IPN in IPNs	DIPN content	Distribution of diisopropylnaphthalenes (mol%)						2,6-DIPN to
(°C)	(h)	(%)	(mol%)	(wt%)	2,6-DIPN	2,7-DIPN	1,3-DIPN	1,6-DIPN	1,7-DIPN	Other	2,7-DIPN ratio
150	0.25	0.1	88.2	0.05	27.0	21.6	21.6	16.2	13.5	n.d.[a]	1.25
	0.5	0.5	89.1	0.2	31.1	23.3	21.0	12.3	12.3	n.d.	1.33
	6	3.0	93.3	1.8	36.1	27.6	18.3	8.0	8.3	1.6	1.31
200	0.02	1.9	89.3	1.1	28.7	24.2	21.3	10.5	11.8	3.4	1.18
	0.5	6.7	93.6	3.1	33.4	29.5	20.0	7.4	7.9	1.8	1.13
	6	19.4	94.3	8.5	37.9	34.6	13.8	6.8	5.5	1.3	1.10
250	0.02	1.8	87.8	0.7	24.2	20.4	20.7	12.7	17.4	4.6	1.19
	0.5	13.2	93.3	6.2	32.9	30.0	17.9	8.5	8.5	2.1	1.10
	6	40.1	93.3	17.3	38.0	39.0	7.9	8.5	5.9	0.9	0.98
300	0.02	11.0	93.2	3.7	33.2	32.3	16.0	8.8	7.7	1.9	1.03
	0.5	40.8	93.1	17.6	38.7	39.7	7.4	7.6	5.7	0.9	0.97
	6	49.5	92.0	16.5	37.0	39.1	7.8	8.4	6.7	1.0	0.95

[a] n.d., not detected.

Table 2
Results of IPN disproportionation over the HM-1 catalyst

Temperature	Time	IPN conversion	2-IPN in IPNs	DIPN content	Distribution of diisopropylnaphthalenes (mol%)						2,6-DIPN to
(°C)	(h)	(%)	(mol%)	(wt%)	2,6-DIPN	2,7-DIPN	1,3-DIPN	1,6-DIPN	1,7-DIPN	Other	2,7-DIPN ratio
150	0.02	0.2	86.3	0.05	36.4	31.0	3.2	10.2	13.9	5.3	1.17
	0.5	2.3	89.0	1.1	41.3	31.5	3.7	8.5	11.1	3.9	1.31
	6	5.0	93.3	2.9	43.6	31.3	4.4	7.4	10.3	3.1	1.39
200	0.02	1.0	86.6	0.5	44.1	32.4	6.8	7.2	7.4	2.1	1.36
	0.5	4.5	89.7	2.5	47.4	30.4	6.2	7.5	6.6	1.8	1.56
	6	19.3	93.7	10.3	48.4	33.2	5.3	7.5	4.7	0.9	1.45
250	0.02	0.7	86.3	0.3	48.9	26.4	6.8	8.6	9.3	n.d.	1.85
	0.5	5.2	88.5	2.6	48.0	28.8	6.9	8.2	6.5	1.6	1.67
	6	26.4	92.9	12.2	44.5	34.2	6.5	8.0	5.7	1.1	1.30
300	0.02	2.5	87.0	1.2	49.3	28.3	5.4	8.5	6.9	1.5	1.74
	0.5	18.2	90.7	7.9	43.7	32.5	6.8	8.9	6.9	0.6	1.35
	6	48.2	91.9	17.5	37.8	38.8	7.5	7.7	7.3	0.6	0.97

Table 3
Results of IPN disproportionation over the HM-2 catalyst

Temperature	Time	IPN conversion	2-IPN in IPNs	DIPN content	Distribution of diisopropylnaphthalenes (mol%)						2,6-DIPN to
(°C)	(h)	(%)	(mol%)	(wt%)	2,6-DIPN	2,7-DIPN	1,3-DIPN	1,6-DIPN	1,7-DIPN	Other	2,7-DIPN ratio
200	0.5	0.1	86.0	0.05	39.3	29.4	12.8	9.6	8.9	n.d.	1.34
	6	0.5	86.3	0.3	45.3	30.4	7.7	10.0	6.7	n.d.	1.49
250	0.02	0.7	86.6	0.4	48.1	26.0	9.2	9.0	7.7	n.d.	1.85
	0.5	2.6	88.5	1.5	53.9	25.7	5.4	8.2	4.9	1.9	2.10
	6	10.9	92.2	5.5	50.2	29.3	5.3	9.1	4.7	1.4	1.71

Table 4
Results of IPN disproportionation over HY zeolite

Temperature	Time	IPN conversion	2-IPN in IPNs	DIPN content	Distribution of diisopropylnaphthalenes (mol%)						2,6-DIPN to
(°C)	(h)	(%)	(mol%)	(wt%)	2,6-DIPN	2,7-DIPN	1,3-DIPN	1,6-DIPN	1,7-DIPN	Other	2,7-DIPN ratio
150	0.5	0.0	86.1	0.0	35.6	43.7	5.7	8.0	6.9	n.d.	0.82
	6	0.3	87.4	0.2	28.4	33.8	4.4	10.9	15.3	7.3	0.84
200	0.02	1.4	87.9	0.6	21.9	30.0	3.5	15.3	21.4	7.8	0.73
	0.5	4.0	93.2	2.4	23.6	38.0	3.1	12.9	16.2	6.2	0.62
	6	25.8	94.6	14.4	36.4	47.5	3.7	6.5	5.0	1.0	0.77
250	0.02	3.0	88.1	1.4	29.5	39.6	3.9	11.2	12.2	3.6	0.74
	0.5	11.2	93.5	5.6	29.7	43.1	3.1	10.3	11.1	2.7	0.69
	6	39.8	93.8	21.1	37.3	45.2	4.7	6.9	5.2	0.6	0.83
300	0.02	5.4	89.7	2.9	18.2	23.9	3.8	15.6	29.9	8.6	0.76
	0.5	39.2	92.5	19.6	37.0	43.0	4.8	6.9	7.1	1.5	0.86
	6	53.6	93.0	20.7	41.1	44.9	4.8	4.8	4.0	0.4	0.92

Table 5
Results of isopropylnaphthalene disproportionation over HB catalyst

Temperature	Time	IPN conversion	2-IPN in IPNs	DIPN content	Distribution of diisopropylnaphthalenes (mol%)						2,6-DIPN to
(°C)	(h)	(%)	(mol%)	(wt%)	2,6-DIPN	2,7-DIPN	1,3-DIPN	1,6-DIPN	1,7-DIPN	Other	2,7-DIPN ratio
150	0.25	0.0	88.1	0.0	31.4	62.7	n.d.	5.9	n.d.	n.d.	0.50
	0.5	0.3	89.2	0.2	26.9	57.1	4.8	6.3	4.8	n.d.	0.47
	6	1.7	94.1	1.0	22.9	66.7	2.5	5.0	2.9	n.d.	0.34
200	0.02	1.7	89.4	1.0	25.1	58.8	4.4	6.3	5.4	n.d.	0.43
	0.5	9.2	94.1	5.3	27.2	58.2	3.8	6.2	4.5	0.1	0.47
	6	29.1	94.6	12.8	31.0	56.0	2.7	5.2	5.0	n.d.	0.55
250	0.02	9.8	91.4	4.4	33.6	48.1	4.4	8.0	5.2	0.7	0.70
	0.5	35.8	93.4	19.2	37.5	45.6	4.0	7.2	5.3	0.5	0.82
	6	48.1	93.9	19.1	38.3	42.3	5.9	7.7	5.3	0.5	0.91

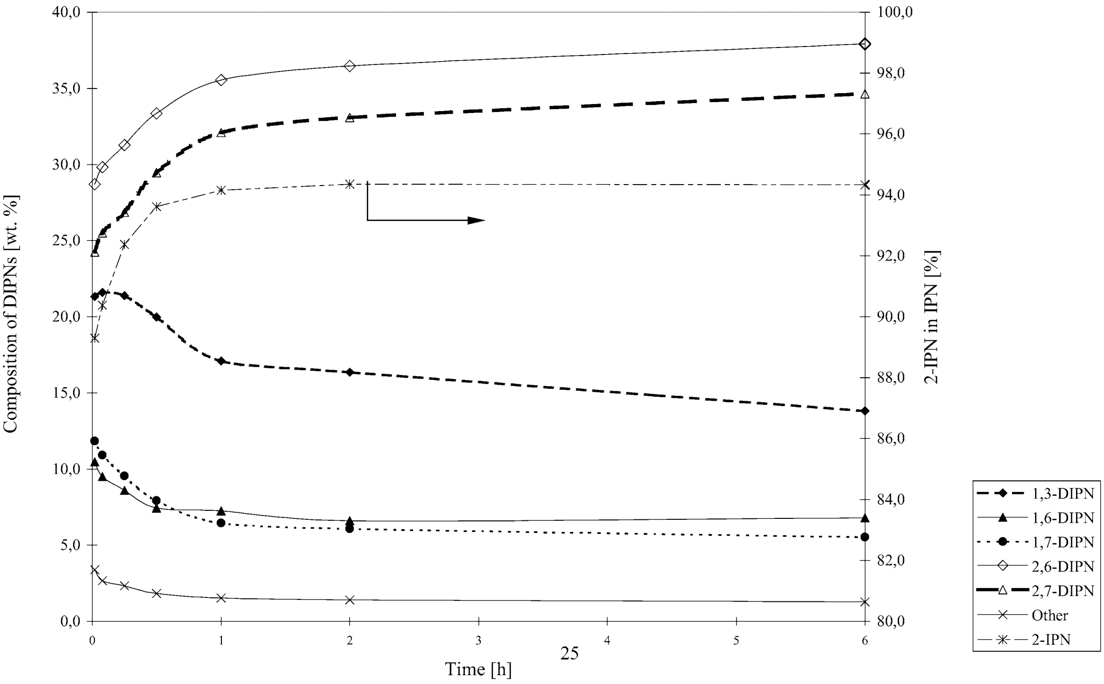

Fig. 1. DIPN isomer distribution in disproportionation product obtained over amorphous aluminosilicate at 200 °C.

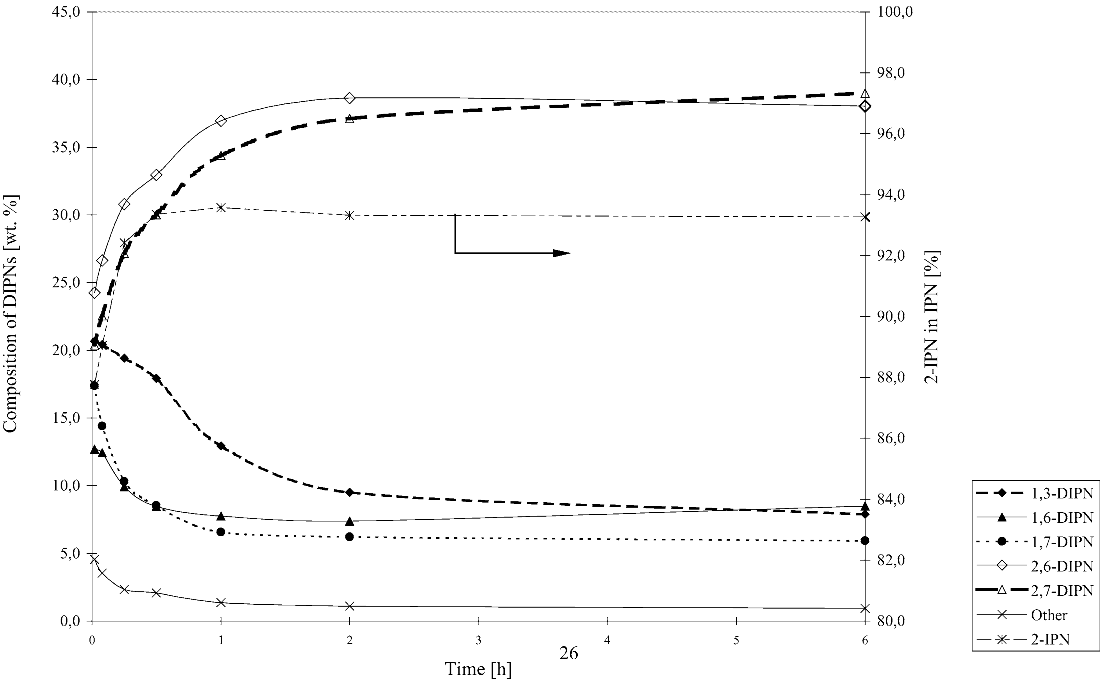

Fig. 2. DIPN isomer distribution in disproportionation product obtained over amorphous aluminosilicate at 250 °C.

are compared. For better illustration of transformations occurring in the reaction system the most characteristic time dependencies of DIPN isomer concentrations are plotted in Figs. 1–5, where results of experiments carried out over AM, HM-1, and HY catalysts at 200 and 250 °C are shown.

As can be seen from Tables 1–5 and Figs. 1–5, for all catalysts, the 2-IPN content in IPN increased with reaction time, and the higher the temperature the more quickly the isomeric composition of IPNs approached equilibrium concentrations.

Also IPN conversion increased with reaction time and the increase was accelerated at elevated temperatures. At the same time, the content of DIPN, naphthalene, triisopropylnaphthalenes, and other alkylnaphthalenes in the recirculated mixture increased. They were mainly produced by disproportionation/transalkylation reactions, although dealky-

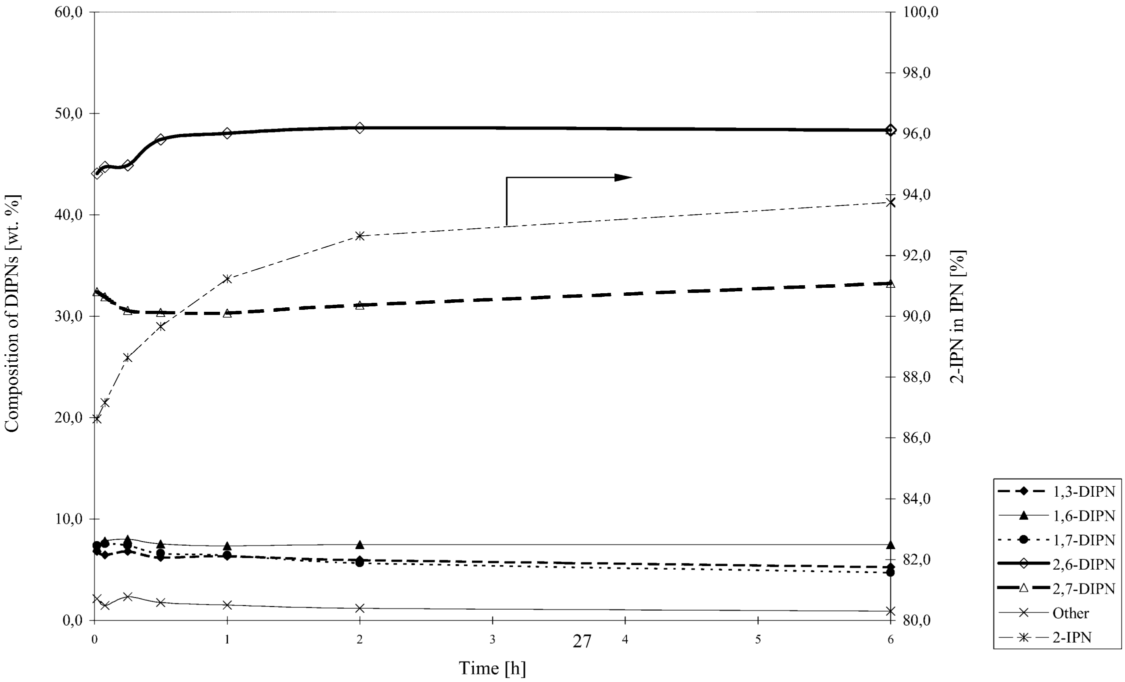

Fig. 3. DIPN isomer distribution in disproportionation product obtained over HM-1 catalyst at 200 °C.

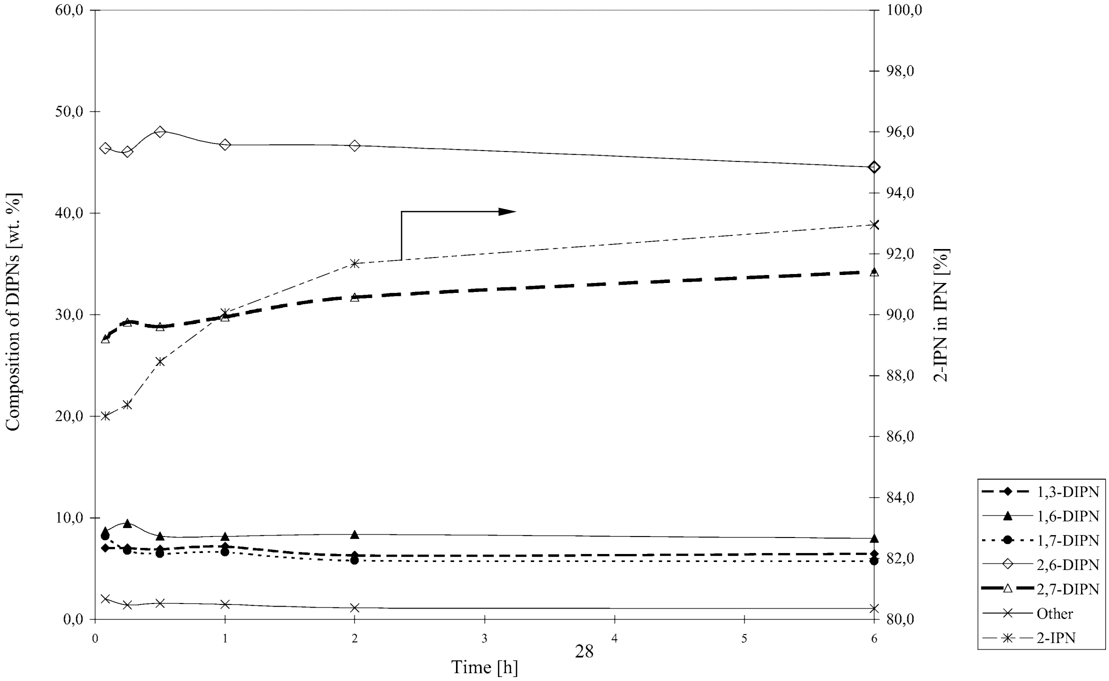

Fig. 4. DIPN isomer distribution in disproportionation product obtained over HM-1 catalyst at 250 °C.

lation and other side reactions were also observed. Especially at high temperature (300 °C) noticeable quantities of propylene and other nonaromatic hydrocarbons were detected in the products. Moreover, other by-products, such as alkylnaphthalenes with other substituents than isopropyl, tetraline, and binaphthyl derivatives, etc. were detected in the products.

As can be seen from Figs. 1 and 2 which show the time dependence of the DIPN isomeric composition in experiments carried out over the AM catalyst at 200 and 250 °C, respectively, concentrations of β,β-isomers (2,6- and 2,7-DIPN) in diisopropylnaphthalene product increased with reaction time and they were the most abundant isomers. Initially the product was rich in α,β-isomers (1,3-, 1,6-, and 1,7-) but they isomerized to the 2,6- and 2,7-DIPN. Distribution of other DIPN isomers (1,4-, 1,5-, and 2,3-) also decreased with reaction time. At high temperatures changes in isomeric composition were more rapid.

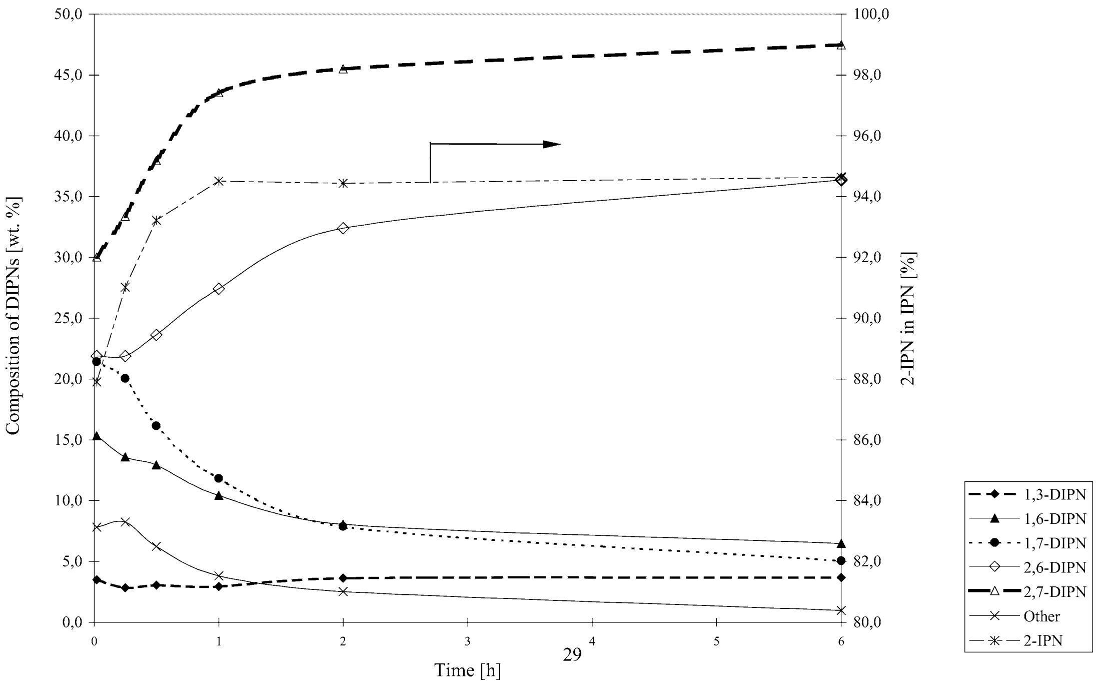

Fig. 5. DIPN isomer distribution in disproportionation product obtained over HY zeolite at 200 °C.

Whereas intramolecular isomerization of 1,6-DIPN to 2,6-DIPN and 1,7-DIPN to 2,7-DIPN is possible, the 1,3-DIPN depletion (simultaneously with 1,4- and 2,3-DIPN) indicates intermolecular isomerization by disproportionation/transalkylation or dealkylation/realkylation-type mechanisms.

In Fig. 2 isomerization of 2,6-DIPN to 2,7-DIPN at 250 °C can be observed. Initially DIPN mixtures contained slightly more 2,6-DIPN than 2,7-DIPN but after 6 h their distribution was reversed. It can be deduced that 2,6-DIPN is kinetically preferred but during further contact with catalyst the mixture composition approaches equilibrium. At thermodynamic equilibrium at 250 °C the distribution of 2,7-DIPN is slightly higher than that of 2,6-DIPN [3]. Therefore, the 2,6-DIPN/2,7-DIPN ratio initially in the range of 1.2–1.3 (see Table 1) decreased with reaction time to 0.95–0.98.

The product of IPN disproportionation over the HM-1 catalyst (Figs. 3 and 4) contained DIPN isomers in descending order: 2,6-DIPN > 2,7-DIPN > 1,3-DIPN ≈ 1,6-DIPN ≈ 1,7-DIPN > other isomers. The distribution of DIPN isomers did not change significantly during the reaction. Similar steady time trends for DIPN concentrations were observed by Sugi and Toba [7] in the alkylation of naphthalene with propylene carried out over mordenite catalysts.

The difference in concentrations of 2,6-DIPN and 2,7-DIPN at 250 °C decreased with reaction time, slowly approaching equilibrium distributions. The initially high 2,6-DIPN/2,7-DIPN ratio (Table 2) of 1.85 decreased to 1.3 due to isomerization and other side reactions. At elevated temperatures the decrease was more apparent and at 300 °C the 2,6-DIPN/2,7-DIPN ratio decreased with reaction time from 1.74 to 0.97. High 2,6-DIPN/2,7-DIPN ratios were also observed over low-silica mordenite HM-2 (Table 3).

Although a 2,6-DIPN/2,7-DIPN ratio higher than 1 can be expected by kinetics (vide AM catalyst), such significant difference in yield of 2,6-DIPN and 2,7-DIPN as that observed over mordenite catalysts indicates shape-selectivity effects. Also, a very low concentration of bulky α, β-isomers, especially 1,3-DIPN, can be attributed to the shape selectivity. From a comparison of the results in Tables 1 and 2 it is evident that the product obtained over the AM catalyst was rich in 1,3-DIPN and its concentration decreased significantly with contact time, whereas the DIPN obtained over HM-1 zeolite was poor in 1,3-isomer, independent of time and temperature. Other bulky isomers (1,6-DIPN and 1,7-DIPN) are also less abundant in the product obtained over the HM-1 than over the AM catalyst.

A different relationship of DIPN isomer concentrations with contact time was observed for zeolite HY (Fig. 5 and Table 4). Although again β, β-isomers were the most abundant in the DIPN mixture, the relation in β, β-isomer contents was inverse to that obtained over HM-1, HM-2, and AM catalysts; i.e., more 2,7-DIPN was formed than 2,6-DIPN. The 2,6-DIPN/2,7-DIPN mole ratio was in the range 0.6–0.9 and preferentially approached the equilibrium value while contacting with the catalyst.

Similarly as for HM-1 catalyst, the formation of 1,3-DIPN was hindered over HY zeolite and its content in the DIPN mixture did not exceed 6%, indicating a shape-selectivity effect. However, 1,6-DIPN and 1,7-DIPN were initially formed over the HY catalyst in quite high concentrations; i.e., comparable to those observed over AM catalyst. Also, other isomers were quite abundant in DIPN mixtures.

All these bulky DIPNs isomerized to the 2,6-DIPN and 2,7-DIPN.

Results of IPN disproportionation over the HB catalyst (Table 5) are similar but clearer than those obtained on the HY zeolite and also indicate shape-selectivity effects. The concentration of bulky 1,3-DIPN, 1,6-DIPN, 1,7-DIPN, and other isomers in the product obtained over HB zeolite was even smaller than that obtained over HM-1 catalyst. 2,7-DIPN and 2,6-DIPN were the most abundant isomers in the DIPN product; however, the 2,6-DIPN/2,7-DIPN ratio was still lower than that observed on HY zeolites and a ratio as low as 0.34 was observed.

Such a small 2,6-DIPN/2,7-DIPN ratio indicates undoubtedly the shape-selectivity effect over HY and HB zeolites. It is not observed over amorphous aluminosilicate and it is out of the range predicted by thermodynamics [3,4] and kinetics [4,11,15] of the reactions occurring in the tested system.

Low concentrations of bulky DIPN isomers and high concentrations of slim 2,6-DIPN and 2,7-DIPN in the products obtained over all tested zeolites can easily be explained by steric hindrances in the pores. However, a question arises why over HB and HY zeolites high selectivity toward 2,7-DIPN is observed but over mordenite catalysts high 2,6-DIPN selectivity occurs. Different acidity of the catalysts seems not to be involved in this difference in selectivity, because 2,6-selectivity was observed both on low and on high-silica mordenites and 2,7-selectivity was observed on low-silica HY and high-silica HB zeolites.

We carefully considered disproportionation mechanisms and sizes of molecules and transition-state complexes and we are able to propose an explanation as follows.

There are two possible mechanisms of isopropylnaphthalene disproportionation. First, the mechanism may be monomolecular, i.e., a dealkylation–realkylation mechanism. Isopropyl substituent (carbocation) abstracted from the IPN molecule alkylates other molecules of IPN to form DIPN. In spatially hindered pores of the tested zeolites the 2-IPN is dealkylated to naphthalene and the abstracted isopropyl substituent attacks the neighbor molecule of 2-IPN at positions 6 or 7 to give respective DIPN isomers. The 2,6-DIPN/2,7-DIPN ratio in the product is expected to be similar to that of alkylation of 2-IPN with propylene. The literature data on naphthalene isopropylation over HY and H-beta zeolites [6,7,16,19,22] indicate that the 2,6-DIPN/2,7-DIPN ratio is higher or close to 1. Also in our experiments on naphthalene alkylation, performed over the same samples of zeolite Y and beta in the same temperature range as disproportionation, a ratio higher or close to 1 was observed. Therefore, high 2,7-DIPN selectivity over HB and HY catalysts cannot be explained by a monomolecular mechanism.

The second possibility is a bimolecular mechanism of disproportionation. Two neighbor molecules of 2-IPN form one huge molecule of intermediate complex by sharing one of the isopropyl groups. Such complex molecules are long and their shape can be strongly influenced by the shape of available void space in the zeolite pores; therefore, this explanation can rationalize the difference for favoring 2,6- or 2,7-DIPN. Schemes shown in Figs. 6 and 7 visualize space-fill models of intermediate complexes leading to 2,6-DIPN and 2,7-DIPN in pores of zeolite Y and mordenite, respectively. Zeolite pores are shown as cross sections of the zeolite lattices. There are possibly several conformers of each transition-state complex; however, the most distinguishing examples of the complexes were chosen to visualize our reasoning. Other conformers (e.g., having mutually perpendicular or crossed planes of naphthalene rings) also seem to obey this way of explanation.

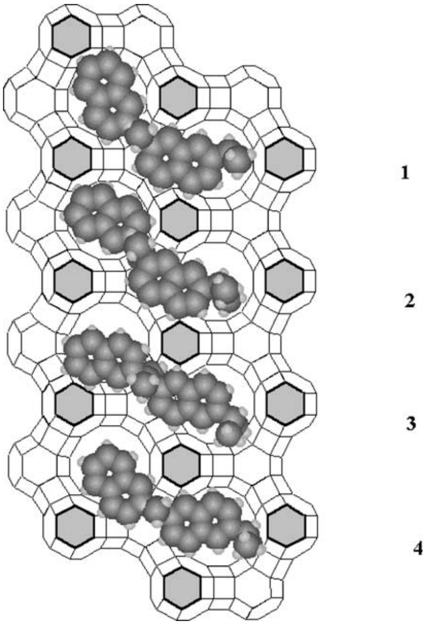

Fig. 6. Scheme of space-fill models of transition-state complexes leading to 2,7-DIPN (1 and 2) and 2,6-DIPN (2 and 3) placed in a cross section of Y zeolite lattice.

The crystalline lattice of Y zeolite creates large void α-cages ca. 1.1 nm in diameter, connected by 12-membered windows of 0.74 nm in diameter [23]. The complex molecules leading to 2,7-DIPN and 2,6-DIPN are ca. 1.8–1.9 and 2 nm long, respectively. There is not enough space in one α-cage of Y zeolite to hold such long molecules. They must occupy partially also the neighbor α-cage through the connecting window. It is evident from Fig. 6 that the molecules of complexes 1 and 2, leading to 2,7-DIPN, are bent and better fit the void space of the Y zeolite than linear molecules of complexes 3 and 4, leading to 2,6-DIPN. It seems that complexes 1 and 2 can be better arranged in the tight window connecting two α-cages of Y zeolite than complexes 3 and 4.

The situation in the mordenite channels is different (Fig. 7) and complexes leading to 2,6-DIPN (3 and 4) better suit the shape of straight channels than complexes leading to 2,7-DIPN (1 and 2).

In other words, the shape of the complex being formed from two IPN molecules depends on the shape of space

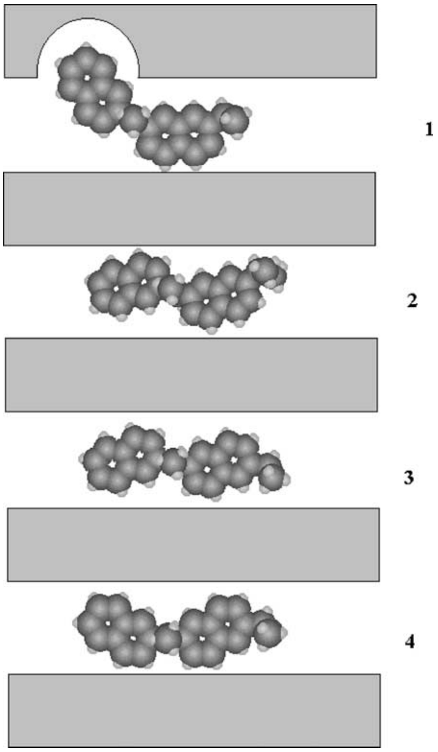

Fig. 7. Scheme of space-fill models of transition-state complexes leading to 2,7-DIPN (1 and 2) and 2,6-DIPN (3 and 4) placed in a cross section of mordenite channels.

available in the pores of zeolites. According to suggestions by Derouane and co-workers [8,25] there are two possibilities that force the complex shape and they both seem to lead to diversity in 2,6-DIPN/2,7-DIPN ratios in pores of different zeolites: first, the constraints in the arrangement of the complex in the pores, and second, based on attractive interactions (responsible for the confinement effect), i.e., matching the shape of the complex to the shape of the pore walls. In HY zeolite pores the complex would be then “wrapped around” the hexagonal prism and sodalite cage, whereas in “straight pipe”-type channels of mordenite the linear complex is preferred.

Although the structure of beta zeolite is frequently not uniform [23] the reason for high 2,7-DIPN selectivity is similar to that described for zeolite Y; i.e., the more bent shape of the transition-state complex better matches the void space in the pores. Apart from straight channels the beta zeolite has perpendicular, intersecting channels which are sinusoidal in shape [24,26]. The complex leading to 2,7-DIPN can be better arranged inside these channels or in the channel intersections than the 2,6-DIPN precursors.

It is also possible that IPN disproportionation (or other bimolecular reactions) influenced 2,7-DIPN selectivity observed by Horsley et al. [8] in the alkylation of naphthalene with propylene over L zeolite. In place of the tilted 2,7-DIPN molecule nested in the side pocket of the L zeolite channel shown in Fig. 5 in Ref. [8], a bent bimolecular complex leading to 2,7-DIPN can be easily located. The complex can be positioned in the channel, along its axis with the bent part of the molecule nested in the pocket.

Composition of the product obtained in the IPN disproportionation is a consequence of many simultaneous reactions and phenomena. The effect of the pore shape on the 2,6-DIPN/2,7-DIPN ratio can be concealed by the non-shape-selective reactions which occur on the external surface of the catalyst as well as by the reactions occurring inside the pores. Such influence is well visible when reaction temperature is changed.

The dominating mechanism of disproportionation varies with temperature. At low temperatures the bimolecular mechanism of disproportionation dominates whereas at high temperatures the monomolecular one dominates [27]. Therefore, at low temperatures, the 2,6-DIPN/2,7-DIPN ratio is strongly influenced by the shape of zeolite pores whereas at 300 °C the 2,6-DIPN/2,7-DIPN ratio approaches thermodynamic equilibrium. A relatively high content of propylene and aliphatics in the products of IPN disproportionation carried out at 300 °C seems to confirm the monomolecular (dealkylation/realkylation) mechanism.

Considering the bimolecular mechanism of disproportionation some comments are necessary to the results of quantum chemical calculations and computer simulations presented by Tasi et al. [4] on page 6516 and linked to Ref. [17]. They stated that intermolecular isomerization of DIPN in the pores of mordenite was impossible because in the transition state of an intermolecular transfer the migrating alkyl group was located between two naphthalene rings and the transition complex was very large [4,17]. This conclusion is in contradiction with our results of IPN disproportionation and also with results obtained in other reactions, e.g., disproportionation of cumene [28] or n-propylbenzene [27] on zeolites, where a bimolecular mechanism was observed. According to the Fig. 7 in Ref. [17], in the case of methyl group transfer between two naphthalene rings the space required for the reaction to proceed is greater than 1.3 nm (assuming 0.15 nm van der Waals radius for carbon atom) and greater than the size of aromatic ring in the plane. In the case of methyl group transfer between two naphthalene rings a space of at least $0.71 \times 0.88 \times 1.3$ nm is required which is larger than any void space available in the mordenite pores. Similarly, the space necessary for bimolecular reactions of benzene alkyl derivatives would be very large.

We must remember that calculations presented by Tasi and co-workers [4,17] simulate two separate alkylnaphthalene molecules reacting in an unhindered environment (without catalyst, solvent, or surrounding molecules) and the arrangement with the lowest possible energy was determined. However, in narrow mordenite channels, while alkylnaphthalene molecules are approaching each other, deformations of bonds connecting protons and alkyl substituents with aromatic ring are possible. In most cases even in an unhindered environment deformations of bonds of reacting molecules can be energetically less demanding than moving bulky molecules to the position with the lowest en-

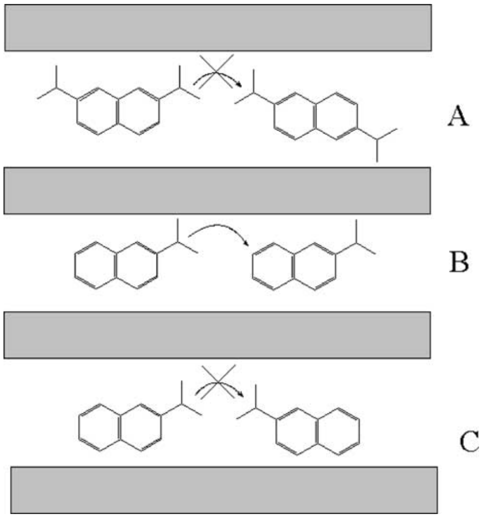

Fig. 8. Scheme of arrangement of neighbor pairs of molecules of β,β-DIPN (A) and 2-IPN (B and C) in mordenite channels. Bimolecular reaction in case A and C is impossible whereas in case B it is feasible.

ergy. Moreover, at high temperatures not only deformations of bonds are common but also bond cleavage is possible. Therefore, in our opinion, the optimization of arrangement of reacting alkylnaphthalene molecules to achieve the lowest energy of the system is not evidence for the lack of a bimolecular mechanism of DIPN isomerization and IPN disproportionation.

An alternative explanation of the possible difficulties in proceeding bimolecular isomerization of DIPNs is shown schematically in Fig. 8. Two molecules of DIPN, reacting in a narrow mordenite channel, have two neighboring alkyl groups which hinder each other to attack a naphthalene ring (Fig. 8A). In Fig. 8B 2-IPN disproportionation is unhindered and the alkyl substituent can be easily transferred between two neighbor naphthalene rings. However, a bimolecular disproportionation is difficult or impossible in mordenite pores if two IPN molecules are arranged to have two alkyl substituents neighboring (Fig. 8C) or no alkyl group between both naphthalene nuclei. In order to enable the bimolecular reaction of DIPN (isomerization, disproportionation, or transalkylation) in the zeolite pores, the presence of the molecule with an easily accessible position in the aromatic ring (naphthalene or IPN) in the surroundings of the DIPN molecule is necessary.

Results of our investigations indicate that IPN disproportionation and other bimolecular reactions can contribute to shape-selectivity effects observed during naphthalene alkylation carried out over zeolites. Relatively high activity of zeolite catalysts in IPN disproportionation and compositions of disproportionation products obtained even at a very short contact time (viz. Tables 1–5) indicate how strongly the product of naphthalene alkylation can be influenced by isomerization and disproportionation.

High 2,6-DIPN/2,7-DIPN ratios observed in the alkylation tests carried out over mordenite catalysts can result from shape selectivity in alkylation as well as from shape selectivity in IPN disproportionation or DIPN isomerization which occurs simultaneously with alkylation. For example, two 2-IPN molecules, formed in the pores by naphthalene alkylation, can disproportionate to naphthalene and β,β-DIPN. The 2,7-DIPN molecule, which diffuses more slowly than the 2,6-DIPN molecule [4,5,8], can undergo intramolecular isomerization to 2,6-DIPN [4] and intermolecular isomerization, i.e., dealkylation/realkylation and disproportionation/transalkylation reactions with neighbor molecules of naphthalene or IPN present in the pores of mordenite. For example, the 2,7-DIPN molecule can disproportionate with neighbor 2-IPN molecule to form 2,6-DIPN or another 2,7-DIPN molecule and 2-IPN (formed from the starting 2,7-DIPN). Such reactions of alkyl substituent transfer between aromatic nuclei can be repeated several times during the migration of this group of molecules through the zeolite pores. The 2,7-DIPN molecule can also transalkylate with neighbor naphthalene molecule to form two molecules of 2-IPN which in turn can disproportionate back to DIPN and naphthalene. If, under given conditions, a bimolecular mechanism of disproportionation prevails over a monomolecular mechanism the product obtained inside mordenite pores is enriched in the 2,6-DIPN whereas those obtained over Y and beta zeolites are enriched in the 2,7-DIPN. It is, therefore, possible that 2,6-DIPN selectivity in alkylation is amplified by the consecutive bimolecular reactions in mordenite pores but is suppressed in pores of other wide pore zeolites.

4. Conclusions

In tests of disproportionation of isopropylnaphthalene carried out over wide pore zeolites high β,β-selectivity in diisopropylnaphthalene product was observed. However, the 2,6-DIPN/2,7-DIPN mole ratio was dependent on the structure of the applied zeolite and on the temperature. Over H-mordenites 2,6-DIPN was the most preferred isomer, whereas 2,7-DIPN was favored over HY and H-beta zeolites.

Such differences in isomer preference can be explained by a bimolecular mechanism of disproportionation. Depending on the zeolite pore architecture the bent transition-state complex, leading to 2,7-DIPN or more linear, leading to 2,6-DIPN, is formed.

Reaction temperature determines which mechanism of disproportionation, monomolecular or bimolecular, is dominate. At low temperatures the bimolecular mechanism of disproportionation is favored whereas at high temperatures the monomolecular one (dealkylation/realkylation) is dominate. In the latter case the 2,6-DIPN/2,7-DIPN mole ratio in the product approaches an equilibrium value.

Relatively high activity of the tested catalysts in IPN disproportionation indicates that secondary reactions can strongly influence the shape-selectivity effect observed in alkylation of naphthalene. In reactions carried out over zeolite catalysts the pore size is not always the most critical factor but the shape of the pores (curvatures, cavities, and pockets) can also play an important role in shape selectivity.

Acknowledgments

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