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Zeolite Pore Entrance Effect on Shape Selectivity in Naphthalene Isopropylation

Robert Brzozowski[1] and Wincenty Skupiński

Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland

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Naphthalene alkylation with propylene was studied over various large-pore zeolites and also over amorphous aluminosilicate catalysts. Isomeric distribution of isopropylnaphthalenes and diisopropylnaphthalenes were compared at different temperatures. Surprisingly, higher α-selectivity in monoalkylation and higher concentration of bulky isomers in diisopropylation was observed in the products obtained over zeolites than over amorphous aluminosilicate catalysts. The explanation of such results was proposed to be a specific shape-selectivity effect of alkylation reaction occurring in the entrances to the pores of zeolite. This type of shape selectivity can be very significant and conceal other shape-selectivity effects such as β-selectivity of reactions occurring inside the pores. Results available from the literature, indicating this type of shape selectivity, were also discussed. © 2002 Elsevier Science (USA)

Key Words: **diisopropylnaphthalene; isopropylnaphthalene; shape selectivity; zeolite; alkylation.**

1. INTRODUCTION

Diisopropylnaphthalene (DIPN) mixture is used as a high-quality solvent for copying materials (1, 2). The 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 (3, 4). Thus, isopropylation of naphthalene over shape-selective catalysts enabling very selective production of 2,6-DIPN is of great interest. Wide-pore zeolites with pore openings restricted by 12-O rings such as mordenite, beta, Y, L, etc., are very promising catalysts for 2,6-DIPN synthesis. High β-selectivity both in mono- and dialkylation carried out over such catalysts can be expected. DIPNs with all substituents in β-positions of naphthalene rings are the slimmest isomers, whereas α, β- and α, α-isomers seem to be too bulky to arise and migrate inside the void space of the catalyst. Also, the critical dimension of 1-isopropylnaphthalene (1-IPN) is greater than that of 2-IPN [0.790 and 0.721 nm, respectively (5)].

A very interesting type of shape selectivity was observed in the alkylation of naphthalene carried out over mordenite catalysts. DIPN products obtained over mordenites contained significantly more 2,6-isomer than 2,7-isomer. Although the 2,6-DIPN and 2,7-DIPN have similar critical diameters [i.e., 0.721 and 0.726 nm, respectively (5)] the 2,6-DIPN/2,7-DIPN ratio in the naphthalene alkylation product was higher than 2 (5–9).

Unfortunately, the majority of publications on the alkylation of naphthalene to DIPNs are focused on the 2,6-DIPN/2,7-DIPN ratio and do not consider other DIPN isomers at all or considered them briefly. Few publications presented isomeric distribution of DIPNs in detail (8–10). However, careful consideration of isomeric distribution of DIPNs can lead to very interesting observations and questions.

DIPNs formed in the alkylation of naphthalene with propylene over the HY and HL zeolites contained only a small percentage of β,β-isomers (2,6-DIPN + 2,7-DIPN) and even 56% of bulky 1,3-DIPN and 1,4-DIPN (8, 9), although high β,β-selectivity in the reaction could be expected. Relatively high β,β-selectivity (64%) was only observed over the HY zeolite at high temperature and long contact time; rather, it was a result of DIPN isomerization than shape selectivity.

More surprising were time dependencies of isomer distributions presented by Sugi and Toba (9). A DIPN product obtained over H-mordenite with silica-to-alumina ratio 11 (HM-11) contained more 1,3-isomer than 2,7-isomer, even though 1,3-DIPN and 1,4-DIPN are the most bulky DIPN isomers. On the other hand, the prevalence of 2,6-DIPN over 2,7-DIPN indicated unambiguously the shape selectivity of the catalyst in the reaction.

Similar discrepancy between expected and obtained distribution of DIPN isomers is observed in other investigations (7, 10–12).

In the alkylation of naphthalene with propylene Brzozowski and Tęcza (11) achieved lower β,β-selectivity over the HY and H-mordenite zeolites than over the amorphous aluminosilicate catalyst, although high β,β-selectivity over amorphous aluminosilicates only follows isomerization reactions. Moreover, the reaction selectivity

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[1] To whom correspondence should be addressed. Fax: +48 22 633 82 95. E-mail: Robert.Brzozowski@ichp.pl.

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to 1,3-DIPN and 1,4-DIPN over the amorphous aluminosilicate was lower than that obtained over shape-selective zeolites.

Song (12) presented results of naphthalene isopropylation over mordenite catalysts with different SiO_2/Al_2O_3 ratio. The *other isomers* (besides the 2,6-DIPN and 2,7-DIPN) constituted more than 50% of the total DIPNs. Even in DIPN mixtures obtained over highly dealuminated mordenites (SiO_2/Al_2O_3 ratio of 110–230) they were present in amount of 9–25%.

Similar to that for DIPNs the discrepancy between expected and obtained β-selectivity in monoisopropylation can be observed. In the alkylation carried out over HM-11 and HM-25 catalysts the bulky 1-isomer was abundant not less than 20–30% in the monoproduct (9). Also, monoisopropylation products obtained over various mordenites with wide spectrum of SiO_2/Al_2O_3 ratio contained a high proportion of the 1-isomer (10–47%) (10, 12).

Moreover, higher β-selectivity of monoalkylation was observed over the amorphous aluminosilicate than over the HY or H-mordenite zeolites (11).

It is difficult to explain such high α-selectivity of naphthalene alkylation over shape-selective catalysts as a result of reactions carried out on the external surface, because usually the external surface constitutes only a small part of the total catalyst surface, and, moreover, both the intracrystalline shape-selectivity effect and the isomerization of mono- and diisopropylnaphthalenes on the external surface lead to the β-selectivity increase in the total process.

Therefore, we performed tests of naphthalene alkylation with propylene over several zeolites and amorphous aluminosilicates at different temperatures with the intent of determining DIPN isomer distribution. We also proposed the explanation of the unusual results described earlier.

2. EXPERIMENTAL

Naphthalene 99.9 wt% pure and propylene 99.6 vol% pure were used as reagents. Three zeolite catalysts of different structure in hydrogen form, viz., mordenite, beta, and Y and two amorphous aluminosilicates with different silica-to-alumina ratio were tested in the alkylation reaction of naphthalene with propylene. Moreover, a sample of Y zeolite in calcium/rare-earth-metal form (CaREY) was tested. Catalyst properties are listed in Table 1.

Dealuminated mordenite and beta zeolite were supplied by Süd-Chemie GmbH (Germany). Y zeolite (EZ-121) was supplied by Engelhard Co. They were used as received. Amorphous aluminosilicate designated as AM1 (PK-200, Solvay Catalysts, Germany) was also used as received. A sample of amorphous aluminosilicate AM2 (SMG) was supplied by Chemical Factory IZC "Mątwy" (Poland). Sodium ions were additionally removed from the AM2 catalyst by washing three times with aqueous solution of ammonia chloride according to the standard method. The CaREY zeolite was obtained by the standard ion exchange of the Na form of Y zeolite with aqueous solution of calcium chloride and followed by three repetitions with aqueous solution of the rare-earth-metal ammonium nitrates (produced by Chemical Factory "Hydromech," Kowary, Poland). Prior to tests each catalyst sample was activated at 500°C in an air stream.

TABLE 1

Properties of Catalysts Tested

Catalyst	Catalyst type	Na_2O content (wt%)	SiO_2/Al_2O_3 mole ratio	BET surface (mg^{-1})
AM1	amorphous aluminosilicate	0.08	13.4	340
AM2	amorphous aluminosilicate	0.06	4.7	395
HM	H form of mordenite	0.0056	84	—
HB	H form of beta zeolite	0.03	25	481
HY	H form of Y zeolite	6.5	5.8	546
CaREY[a]	Calcium/rare-earth-metal form of Y zeolite	2.1	4.9	—

[a] Weight percent content of elements as oxides: $CaO = 2.2\%$, $RE_2O_3 = 4.9\%$ (RE_2O_3 = a mixture of 33% La_2O_3, 8% CeO_2, 17% Pr_6O_{11}, and 38% Nd_2O_3).

Alkylation was carried out in a continuous fixed-bed reactor (5 g of catalyst) at 3.0 MPa, at FW = 9 g/g of catalyst/h. The naphthalene-to-propylene mole ratio of 1.5/1 was maintained. The experimental method and apparatus are more precisely described elsewhere (11).

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 (13).

3. RESULTS AND DISCUSSION

Results of the experiments on naphthalene alkylation with propylene carried out at three different temperatures, namely 150, 200, and 250°C, over various aluminosilicate catalysts are summarized in Table 2. Results such as the propylene conversion, the 2-IPN content in total monoisopropylnaphthalenes and the isomeric distribution of DIPNs are compared. Experimental results are also compared with those at thermodynamic equilibrium at 250°C available from the literature (14). Two main groups of DIPN isomers are distinguished. The first group (2NR-DIPN) includes isomers with each isopropyl substituent attached to a different naphthalene ring (i.e., 1,5-; 1,6-; 1,7-; 2,6-; and 2,7-DIPN) and the second group (1NR-DIPN) includes isomers with both isopropyl substituents attached to the same naphthalene ring (i.e., 1,4-; 1,3-; and 2,3-DIPN). Moreover, within each group, DIPN isomers are divided into β,β-isomers (2,6-DIPN + 2,7-DIPN),

TABLE 2

Results of Naphthalene Alkylation with Propylene over Different Catalysts

Catalyst and alkylation temperature (°C)	Propylene conversion (wt%)	2-IPN/ IPN (%)	2NR-DIPN isomers (%)				1NR-DIPN isomers (%)		
			2,6 + 2,7	1,6 + 1,7	1,5	Σ 2NR-DIPN	1,3	1,4	Σ 1NR-DIPN
Equilibrium at 250°C[a]	—	93.3	77.0	14.5	0.2	91.7	7.6	0.2	8.3
AM1									
150	3.5	33.2	20.5	27.6	11.1	59.2	21.8	18.5	40.8
200	44.7	74.3	45.6	21.1	2.9	69.6	24.9	4.5	30.4
250	85.8	91.0	69.8	14.8	0.7	85.3	13.0	1.0	14.7
AM2									
150	69.7	36.5	16.9	28.3	9.9	55.1	23.6	20.1	44.9
200	96.3	84.2	66.0	13.3	0.7	80.0	18.2	1.0	20.0
250	96.1	89.5	74.3	13.7	0.4	88.4	10.6	0.5	11.7
HB									
150	3.7	44.9	47.9	24.2	6.2	78.3	8.9	12.9	21.7
200	48.4	50.4	33.2	27.8	6.6	67.6	18.0	13.5	32.4
250	83.8	80.0	61.5	19.4	1.4	82.3	14.5	2.4	17.7
HY									
150	2.5	27.8	58.8	27.9	0.0	86.7	13.2	0.0	13.3
200	44.9	47.5	24.3	38.7	7.5	70.5	12.0	15.3	29.5
250	96.3	85.6	55.6	25.2	1.7	82.5	12.5	3.1	17.5
HM									
150	2.9	52.1	56.4	18.5	4.4	79.3	13.2	7.5	20.7
200	17.9	49.5	33.7	28.9	7.8	70.4	12.6	16.2	29.6
250	75.3	74.6	63.6	19.5	2.9	86.0	10.2	2.9	14.0
CaREY									
150	1.9	65.0	43.7	25.0	6.3	75.0	12.5	12.5	25.0
200	31.3	32.1	4.6	29.1	9.7	43.4	12.3	44.0	56.6
250	95.8	50.5	16.1	33.3	7.8	57.2	24.5	17.5	42.8

[a] Thermodynamical equilibrium (14).

α,β-isomers (1,6-DIPN + 1,7-DIPN and 1,3-DIPN) and α,α-isomers (1,5-DIPN and 1,4-DIPN). The intramolecular isomerization, which always accompanies the alkylation reaction, can change proportions of DIPN isomers inside the group 1NR-DIPN or 2NR-DIPN, which increases the population of isomers with isopropyl substituents at β-positions at the expense of isomers with substituents at α-positions. On the other hand, only the intermolecular isomerization can change proportions between isomers from groups 1NR-DIPN and 2NR-DIPN, preferentially increasing distribution of 2NR-DIPN isomers.

As can be seen from Table 2, at a temperature of 150°C all the catalysts tested in naphthalene alkylation with propylene, except for AM2, revealed very low propylene conversion. However, in all cases the increase of reaction temperature led to a significant increase in propylene conversion.

Over non-shape-selective amorphous aluminosilicates AM1 and AM2, the 2-IPN content in monoisopropylnaphthalenes rose very quickly with temperature increase as a result of more intensive isomerization and at 250°C it approached nearly equilibrium value. Similarly, the distribution of DIPN isomers approached thermodynamic equilibrium with the reaction temperature increase. The intramolecular isomerization increased β,β-selectivity in the product and the summary content of 2,6-DIPN and 2,7-DIPN increased from 17–20.5% to 70–74%, whereas the content of 1,5-DIPN decreased from 10–11% to less than 1%. Also, the 1,4-DIPN content dropped from 18.5–20% to 0.5–1%.

The intermolecular isomerization over amorphous aluminosilicates is easily discerned. 2NR-DIPN content increased with the temperature increase from 55–59% to 85–88%, whereas 1NR-DIPN isomers content decreased from 41–45% to 12–15%.

Visibility of intramolecular isomerization within the 1NR-DIPN group was disrupted by two factors. First, the 2,3-DIPN content in the product was lowered by the steric hindrances of two bulky, adjacent substituents in the molecule. Second, the intramolecular isomerization of 1,4-isomer to 1,3-isomer was strongly affected by the intermolecular isomerization. Thus, in most cases, the 1,3-DIPN content (and also 1NR-DIPN) in the product dropped with the temperature increase. It rose only when alkylation temperature was increased from 150 to 200°C in the reaction carried out over AM1 amorphous aluminosilicate.

Evidently different results were obtained over zeolite catalysts. Over the HB and HY zeolites β-selectivity of monoalkylation rose very slightly with temperature increase from 150 to 200°C compared to amorphous aluminosilicates and over the HM and CaREY it dropped.

Especially high drop of 2-IPN distribution in IPN (from 65 to 32%) was observed for the CaREY zeolite. Further temperature increase, however, was followed by β-selectivity increase for all zeolites tested.

More evident than for the monoalkylation, the drop of β-selectivity with temperature increase from 150 to 200°C was observed for the dialkylation of naphthalene. For all zeolites tested, the 2,6-DIPN and 2,7-DIPN content decreased from 40–60% to 20–30% and for the CaREY as low as 4.6%. Moreover, the content of 2NR-DIPN isomers in the product decreased whereas that of 1NR-DIPN increased.

The alkylation temperature increase from 200 to 250°C increased velocities of both isomerizations and, as a result, increased β,β-selectivity and distribution of 2NR-DIPN isomers in DIPN mixtures.

The results of naphthalene alkylation with propylene obtained over the CaREY zeolite are especially worthy of emphasis. The product obtained at 200°C contained as little as 4.6% of 2,6- and 2,7-DIPN's and as much as 56.6% bulky 1NR-DIPN isomers. Such amazing concentration of these isomers did not occur for any alkylation product obtained over any other catalyst at any temperature.

The preceeding experimental results are very surprising with regard to shape selectivity of zeolite catalysts. If we compare pore dimensions of the tested zeolites with the critical diameter of each DIPN isomer, a very high β-selectivity of the alkylation reaction inside the zeolite pores is expected. Critical diameters of the 2,6- and 2,7-DIPN are not greater than 0.726 nm, whereas those of 1,3-DIPN and 1,4-DIPN are 0.934 and 0.9 nm, respectively. Also, the product formed on the external surface of the zeolite should be at least as rich in 2-IPN and β,β-DIPNs as that obtained over the amorphous aluminosilicate catalysts. It is common knowledge that zeolites have higher acidity than amorphous aluminosilicates, therefore, even more intensive isomerization on the external surface of the zeolite can be expected and, as a result, higher β-selectivity of alkylation.

In our opinion such contradiction between the expected and obtained results of the naphthalene alkylation with propylene over zeolite catalysts can be explained considering that the alkylation and the reactions accompanying alkylation can occur in a specific way in the pore entrances. Great importance of active sites placed at the entrances was already proposed in the literature on catalysis, for example, by Derouane (15) for the cracking of *n*-paraffins (the nest effect) and by Fraenkel *et al.* (16) for the naphthalene alkylation with methanol.

According to our proposition, the naphthalene molecule is adsorbed in the pore entrance in the way shown in Fig. 1, i.e., it is partially located inside the channel along the channel axis. Figure 1 shows the 1,4-DIPN molecule adsorbed in the pore entrance which had been formed from the naphthalene molecule. The adsorbed naphthalene molecule can react with the propylene carbocation formed previously or simultaneously on active sites at or near the pore entrance.

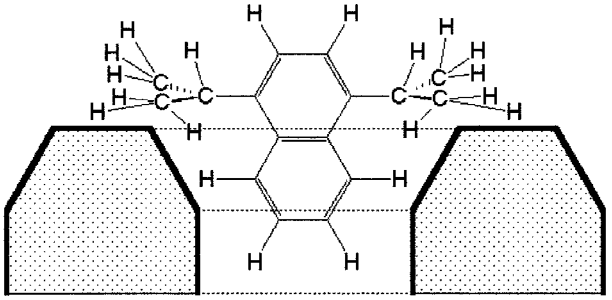

FIG. 1. Scheme of arrangement of the 1,4-DIPN molecule formed from the naphthalene molecule by isopropylation in the zeolite pore entrances.

A substitution at the α-position of the naphthalene molecule adsorbed in the pore entrance is preferred both according to the alkylation mechanism and because the α-position is closer to the olefin molecule adsorbed on the external surface than the β-position. Therefore, 1-IPN in the case of monoalkylation and 1,4-DIPN in the case of diisopropylation are the most preferred products.

The alkylated naphthalene molecules obstruct channels for substrates entering and products leaving pores and, therefore, the catalyst crystallite interior is impoverished in propylene. The propylene concentration in the space outside the zeolite crystallite becomes much higher than that inside pores and additionally favors increase of 1NR-DIPN isomers.

The most probable reactions of the 1-IPN molecule adsorbed in the pore entrance are further alkylation to 1,4-DIPN or 1,3-DIPN or isomerization to 2-IPN (and further alkylation to 1,3-DIPN). The alkylation of the molecule at positions 6 and 7 is less probable due to lower concentration of propylene inside pores. Moreover, the substitution of the adsorbed 1-IPN or 2-IPN molecule at more kinetically preferred α-positions (5 and 8) is excluded and hence formation of the 1,5-, 1,6-, and 1,7-DIPNs (i.e., 2,6-DIPN and 2,7-DIPN precursors) is impossible. Although formation of 2NR-DIPN isomers inside the pores is not excluded they can be formed mainly by consecutive reactions of the products formed in the pore entrances (e.g., alkylation of IPN, intermolecular isomerization of 1NR-DIPNs, transalkylation of polyisopropylnaphthalenes) occurring on the external surface of catalyst, amorphous admixtures, crystalline lattice defects, etc.

To explain temperature influence on our experimental results we assumed that all reactions can run on active sites located at three different places on the zeolite crystals: on the external surface, in the entrances to the channels, and entirely inside the pores or cavities of zeolite. The resultant product is, therefore, a mixture of three different products, the proportions of which can be varied by changing the process conditions.

Thus, at a relatively low temperature of 150°C, while diffusion through the pores of the zeolite is slow and the naphthalene or alkylnaphthalene molecules are relatively strongly adsorbed in the pore entrances, the resultant product is rich in products obtained on a *truly* external surface. The propylene conversion is low and isomeric distribution of the product indicates lack of shape selectivity. The β-selectivity is then rather a result of isomerization on the external surface.

At temperature increased to 200°C desorption of molecules from the pore entrances becomes much easier and the product formed in the entrances prevails in the resultant product. However, products formed inside the pores of the zeolite also can be very significant in the resultant product and various effects can be observed simultaneously. For example, in our product obtained over the HM catalyst both a high 2,6-DIPN/2,7-DIPN ratio (>1.4) and high 1NR-DIPN content were observed. Similar observations are also available from the literature (9).

At 250°C the molecules adsorbed in the pore entrances are easily desorbed and enable other molecules to migrate into and from the pores quite easily. The mobility of hydrocarbon molecules at higher temperature is increased and vibrations of atoms in the zeolite lattice are more intensive, which leads to greater fluctuation in the pore diameter. Therefore, the effect of the pore entrances becomes less visible and the resultant product appears significantly enriched in the products formed entirely inside the pores.

Proportion between products obtained according to both types of shape selectivity (i.e., intracrystalline and in pore entrances) seems to depend strongly not only on the temperature of the reaction but on properties of the catalyst as well. The CaREY zeolite is expected to have narrower windows leading to α-cavities than the HY zeolite because ionic radii of calcium and rare-earth metals are at least two times greater than the radius of hydrogen (17). Therefore, the product obtained at 200°C over the CaREY catalyst is enriched in the 1NR-DIPN isomers (especially in 1,4-DIPN) if compared with the product obtained over the HY zeolite.

Our theory reasonably explains not only our experimental results but also the results of naphthalene isopropylation available from the literature and described in the introduction section. The effect of pore entrances concealed other shape selectivity effects and, therefore, high α-selectivity and high 1NR selectivity in the naphthalene alkylation over the shape-selective catalysts were observed simultaneously with a high 2,6-DIPN/2,7-DIPN ratio.

Our theory also seems compatible with observations that the dealumination of mordenites improves their shape selectivity and as a result the 2,6-DIPN/2,7-DIPN ratio increases in the alkylation product (9, 12, 18). Apart from deactivation of the external surface the dealumination widens pores of the zeolite and the entrance effect becomes less influential; the resultant product is then highly enriched in the shape-selective product formed inside the zeolite pores. Similarly, a covering of the external surface of the zeolite with metals, silanation, etc. (19, 20), can eliminate or decrease the effect of catalysis in the pore entrances.

The shape selectivity effect of pore entrances can also be responsible for abundance of triisopropylnaphthalenes (TIPNs) in the naphthalene alkylation product. Two basic ways are possible. First, the 1,4-DIPN or 1,3-DIPN molecule adsorbed in the pore entrance can be isopropylated (alkylated or transalkylated from the interior of the crystallite) at positions 6 or 7 to 1,3,6-TIPN, 1,3,7-TIPN, or 1,4,6-TIPN. Second, the 2-IPN or any 2NR-DIPN isomer molecule adsorbed in the pore entrance with the isopropyl substituent at the β-position directed toward the interior of the zeolite crystallite can be easily alkylated to TIPN by the olefin molecule from the exterior. There are available literature data where products obtained over highly shape-selective catalysts contained at least several percent of tri- or polyisopropylnaphthalenes (7, 12, 18, 20).

Unusually high TIPN yield in shape-selective catalysis seems to be more evident in the experiments of 2,6-DIPN alkylation with propylene performed and precisely balanced by Schmitz and Song (21). In the experiment carried out over the mordenite catalyst with SiO_2/Al_2O_3 ratio 14 (HM-14) at a propylene-to-2,6-DIPN mole ratio of 0.5 the distribution of 2,7-DIPN and other DIPNs increased only by 0.7 and 4.3%, respectively, whereas that of TIPN and tetraisopropylnaphthalene (TeIPN) increased by 18.9 and 1.9%, respectively. According to the traditional point of view that shape-selective reactions run exclusively inside the pores whereas on the external surface of the zeolite only non-shape-selective reactions are possible such results are very surprising. The main reaction expected inside the pores is isomerization of 2,6-DIPN to 2,7-DIPN whereas on the external surface the increase in *other DIPN* content in the extent similar or even higher than that for TIPN should be expected.

In the reaction of the feed with a propylene-to-2,6-DIPN mole ratio of 4.0 carried out over the HM-14 zeolite, the distribution of all monoisopropylnaphthalenes, 2,6-DIPN, and 2,7-DIPN fell and other DIPNs remained unchanged, whereas the content of TIPN and TeIPN increased by 25.9 and 3.7%, respectively (21). Please note that the TIPN distribution in the product was several times greater than that of the TeIPN, although a very significant excess of propylene was applied (6 mol of propylene or isopropyl substituents to 1 naphthalene molecule). In non-shape-selective catalysis such reaction conditions should prefer the TeIPN over the TIPN because in the unhindered environment the TIPN molecule is easily alkylated to the TeIPN. However, the preceding experimental results are more consistent with our theory. The TeIPN formation from the TIPN in the pore entrance is impossible because the only positions unoccupied by alkyl substituents of the TIPN nucleus are not available for the alkylating agent.

In the reaction carried out over highly shape-selective dealuminated mordenite HM-74 changes in distribution of IPNs and DIPNs are less significant than the formation of TIPN (21). For the feed with propylene-to-2,6-DIPN mole ratio of 0.5 the 2,6-DIPN amount in the product increased by 1.4% at the expense of monoisopropylnaphthalenes and/or 2,7-DIPN and other DIPNs. Simultaneously, the distribution of TIPN and TeIPN rose by 2.2 and 0.2%, respectively. The reaction of the feed with propylene-to-2,6-DIPN mole ratio of 4.0 over the HM-74 zeolite led to decrease of all mono- and diisopropylnaphthalenes in the product whereas the content of TIPN and TeIPN rose by 4.2 and 0.5%, respectively.

Other observations and careful considerations of available literature data are also consistent with our theory. Moreau *et al.* (22) recently described the presence of a large amount of alkyl-indane-type derivative of naphthalene (2,3-dihydro-1,1,3-trimethyl-1H-benz[f]indene) in the alkylation product obtained over H-beta, HY, and H-mordenite zeolites. Rise (except for α-cages of the HY) and diffusion of such a bulky molecule through the pores of the zeolites seems impossible. On the other hand, *immobilization* of the reacting naphthalene molecule by adsorption in the entrance to the pore can enhance mechanisms of arising of this compound, both that proposed by Moreau and co-workers as well as a mechanism via isomerization of 1,3-DIPN to 2,3-DIPN and subsequent dehydrogenation to the indane-type naphthalene derivative.

Apart from the isopropylation of naphthalene, there are available literature data indicating shape selectivity of the pore entrances in the reactions carried out with other alkylating agents. Quite significant α-selectivity and 1NR selectivity were observed in the products of naphthalene alkylation with ethylene (23) and methanol (16) carried out over shape-selective zeolite catalysts.

4. CONCLUSIONS

The shape-selectivity effect that occurred in the entrances to the pores can be responsible for both high α-selectivity in monoisopropylation and 1NR-selectivity in diisopropylation observed in the naphthalene alkylation over wide pore zeolites; the product is then relatively rich in 1-IPN, 1,3-DIPN, and 1,4-DIPN. This type of shape selectivity conceals other shape-selectivity effects such as high β-selectivity of reactions occurring inside channels or cavities of the zeolite.

Moreover, high concentration of TIPNs in alkylation products can be explained superbly with the help of catalysis in pore entrances.

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