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Dialkylation of naphthalene with isopropanol over acidic zeolites Influence of pore structure on selectivity

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Abstract

The liquid phase alkylation of naphthalene with isopropanol has been studied over various large pore zeolites with intermediate aluminum content. While H-Y zeolite exhibits the best activity, and shows a high selectivity in 2,6- and 2,7-diisopropylnaphthalenes, in agreement with previous studies, H-Beta displays a peculiar behavior under the same conditions. The latter produces little diisopropylnaphthalenes; instead, a series of unexpected compounds, consisting of (cyclopentyl)naphthalene derivatives (so-called cyclizates), are formed in high yields. H-Mordenite, which features low activity, also demonstrates such an unexpected behavior towards formation of multialkylated products. The results obtained over H-Beta are more particularly reported, and the identification of the cyclizates is confirmed. A mechanism is proposed to explain the formation of these compounds depending on the various catalytic materials used, and the impact of the pore structure on activity and product distribution is discussed.

Keywords: Zeolites; Shape-selective catalysis; Naphthalene isopropylation

1. Introduction

In the past decade, shape-selective naphthalene alkylation of polynuclear aromatic hydrocarbons, especially naphthalene and biphenyl, has received considerable attention due to the demand for the corresponding symmetrically substituted dialkyl derivatives, such as 2,6-diisopropylnaphthalene and 4,4′-diisopropylbiphenyl. For example, 2,6-dialkylnaphthalenes, as precursors of 2,6-naphthalene carboxylic acid, turned to be very important building blocks in the preparation of advanced polymer materials displaying high thermal and mechanical stability, such as poly(ethylenenaphthalate), or thermotropic liquid crystal properties [1,2]. Zeolites have been extensively studied for the alkylation of mononuclear aromatic hydrocarbons, and proved to be promising solids for achieving highly shape-selective catalysis [3–5]. The use of medium and large pore size zeolites for naphthalene and biphenyl alkylation has then gained increasing importance as reported in recent reviews [6–8]. The gas phase alkylation of naphthalene with methanol has been first investigated over H-ZSM-5, H-Mordenites and H-Y zeolites [9–11]; medium pore H-ZSM-5 showed a high so-called

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β-selectivity, but only moderate activity. More attention has recently been paid to large pore zeolites, such as H-Mordenites, H-Y, H-Beta, and in the last three years, to mesoporous aluminosilicates, while alkylating agents of large steric hindrance such as isopropanol [12–16], propene [12,17–25], isopropylbromide [26], cyclohexyl bromide and cyclohexene [27–30], *tert*-butanol [31–33], have been applied successfully to the selective syntheses of 2,6-dialkylnaphthalenes. Among these various studies, substantial advances have been obtained in naphthalene isopropylation for both the understanding of the alkylation mechanism and the design of catalysts leading to a high selectivity in 2,6-diisopropylnaphthalene (DIPN). Katayama et al. [12] first reported studies on the catalytic behaviors of H-Y, H-L, H-Mordenites and H-ZSM-5 in the alkylation with propene or isopropanol in batch conditions, disclosing the higher selectivity of H-Mordenite for 2,6-DIPN over other zeolite types. Sugi et al. [7,19,21,22] have made remarkable progress in improving the performance of H-Mordenites for selective preparation of 2,6-DIPN by dealumination or metallic modifications, while Song et al. [13,23,24] have shown that the addition of small amounts of water could be beneficial for both improving 2,6-DIPN selectivity and decreasing coking of the catalyst. On the other hand, the results obtained in our group [26–32] indicate that H-Y is a better catalyst than H-Mordenite or H-Beta for the selective synthesis of 2,6-dialkylnaphthalenes in the liquid phase isopropylation, cyclohexylation or *tert*-butylation, in terms of activity and β,β′ selectivity. These results are in agreement with the conclusions reached by Chu and Chen [14], who carried out the isopropylation reaction in a continuous fixed-bed reactor. However, when the reaction is carried out, over H-Y zeolites, in a flow reactor under high temperature and pressure conditions, the isopropylation of naphthalene is accompanied by a certain number of side reactions, such as oligomerization and cracking together with isomerization of the main diisopropylnaphthalene derivatives [34]. Mesoporous aluminosilicates have also been found to be active in the isopropylation of naphthalene, and selective in 2-IPN (2-isopropylnaphthalene) and 2,6-DIPN. On the other hand, H-Beta zeolite, a three-dimensional 12-ring structure [35,36], has been found to be more active and selective than H-Y for the preparation of cumene in the alkylation of benzene with propene [37]. Nevertheless, such a catalyst has not been shown to possess a catalytic uniqueness in the alkylation of polyaromatics [14,16,31–33], and only little attention has been paid to its application in the isopropylation reaction of naphthalene [14,16]. However, the unusual formation of sec-butylbenzene and isobutylbenzene instead of the expected *tert*-butylbenzene was recently observed in the butylation of benzene with isobutanol over zeolite H-Beta [38].

In our search for suitable catalysts for the selective synthesis of 2,6-dialkylnaphthalenes, we found that H-Beta displayed a peculiar catalytic behavior in the liquid phase alkylation of naphthalene with isopropanol [39]. Thus, under given conditions, a series of new compounds, consisting of (cyclopentyl)-naphthalene derivatives (cyclizates hereafter), were formed with high selectivity, while they were obtained in much smaller amounts over H-Y. Our studies have been extended to H-Mordenite, which also demonstrated such an unexpected behavior for the formation of the multialkylated products.

The present paper deals with the unusual results thus obtained and the mechanism of the formation of the cyclizates in the alkylation of naphthalene with isopropanol in relation with the pore structure of the various catalysts used.

2. Experimental

2.1. Catalysts and reactants

The H-Beta (12.5) sample was obtained from PQ Corporation (CP 810 B-25, H-form). H-Y (15) and H-Mordenite (10.8) were obtained from Zeocat, Montoir de Bretagne (ZF515 and ZM510, respectively). The properties of the catalysts are listed in Table 1. The calcination was performed at 773 K for 5 h with a heating rate of $60\,K\,h^{-1}$ from RT to 773 K. All the calcinations were performed in a flow of dry air.

Analytical grade isopropanol, naphthalene (Aldrich Company), undecane (internal standard) and cyclohexane were used without purification.

2.2. Catalytic runs

The reaction was carried out in a 0.16 l stirred autoclave reactor (Parr Instrument Company). In a

Table 1
Properties of zeolite catalysts

Catalyst	Si/Al	BEF surface area ($m^2\,g^{-1}$)	Pore architecture according to [40]
H-Y (15)	15	762	Large cavities (∅ 13 Å) interconnected by 0.74 nm windows
H-Beta (12.5)	12.5	658	Interconnected channels with pore opening of 0.55 nm × 0.55 nm and 0.76 nm × 0.64 nm
H-Mordenite (10.8)	10.8	510	Unidimensional channels with opening of 0.65 nm × 0.70 nm and side pockets of 0.26 nm × 0.57 nm

typical experiment, naphthalene (1.28 g, 10 mmol), isopropanol (1.22 g, 20 mmol), undecane (1.56 g, 10 mmol) as an internal standard sample and 100 ml of cyclohexane as solvent were mixed together in the autoclave; the zeolite (0.50 g), freshly calcinated and kept at 473 K under dry air atmosphere, was then added. The autoclave was sealed and flushed with N_2 several times to replace the air. Reaction temperature was set at 473 K. For all reaction runs, the pressure was controlled at 2 MPa with nitrogen. Reaction conditions other than typical or standard are shown on tables or/and figures.

2.3. Product analysis and identification

The samples were withdrawn periodically from the autoclave and analyzed on a Varian Series 30 gas chromatograph equipped with HP-5 capillary column (25 m) and FID detector. The analysis program was 373–553 K at 10 K min^{-1} heating rate. GC–MS (HP 5970) with OV1 capillary column (25 m) and NMR (Brüker AC200) were used for identification of the products. The conversion was calculated on the basis of the amount of naphthalene converted.

3. Results and discussion

3.1. Unusual results of naphthalene isopropylation over zeolite H-Beta

Typical reaction results in the alkylation of naphthalene with isopropanol over H-Y, H-Beta, and H-Mordenite zeolites, respectively, are listed in Table 2.

Table 2 shows that unexpected (cyclizates) compounds are especially formed with high selectivity over H-Beta. As reported in our preliminary paper [39], product identification has been achieved by combining the data from GC, GC–MS and ^{13}C NMR analysis. It has been especially shown that the molecular mass (*m*/*z*) of these products (210, 252, 292) are different from those of the classical isopropylnaphthalene derivatives (IPN 170, DIPN 212, TIPN 254, TetIPN 296). Fig. 1, which gives typical

Table 2
Reaction results of isopropylation of naphthalene over different zeolites at 473 K[a]

Catalyst (Si/Al)	Reaction time (h)	Naphthalene conversion (%)	Product distribution (mol%)					Distribution of cyclizates with *m*/*z* (mol%)			
			IPN	DIPN	TIPN	Cyclizates	Others[b]	210	252	292	294
H-Y	1	92.3	36.9	41.1	14.7	5.9	1.4	0	88.9	0	11.1
(15)	7	94.6	31.1	46.2	14.2	7.1	1.4	0	91.7	0	8.3
H-Beta	1	18.7	49.6	2.6	0	46.3	1.5	86.2	10.8	2.8	0
(12.5)	7	28.5	42.6	3.1	0	48.1	6.2	84.0	10.2	6.0	0
H-Mordenite	1	13.6	86.3	3.8	0	9.9	0	100	0	0	0
(10.8)	7	19.0	80.2	5.7	0	12.8	1.3	100	0	0	0

[a] Reaction conditions: catalyst 0.50 g, naphthalene 10 mmol, isopropanol 20 mmol, undecane 10 mmol, solvent cyclohexane 100 ml, 2 MPa.
[b] Others include methyl-isopropylnaphthalene and ethyl-isopropylnaphthalene.

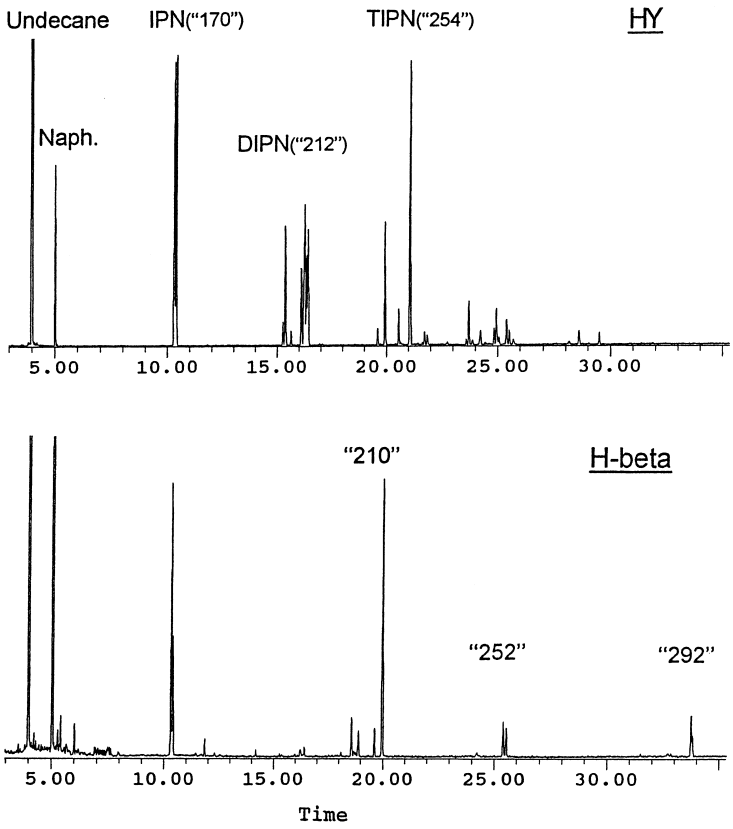


Fig. 1. Chromatograms of typical isopropylation products obtained over H-Y and H-Beta.

gas chromatograms of the products obtained from naphthalene isopropylation over H-Y and H-Beta, respectively, highlights the strong difference in the catalytic behavior of the two zeolites.

The identification procedure is confirmed here by the ^{13}C NMR spectrum (Fig. 2) of the main "210" isomer, which is consistent with the (trimethylcyclopentyl)naphthalene structure depicted in Fig. 3, in agreement with spectral data of related derivatives [41].

It can be seen from Table 2 that the activities of H-Beta and H-Mordenite are much lower than that of H-Y, as shown by the naphthalene conversions which reach a maximum of 30 and 20%, respectively, under standard reaction conditions for the former zeolites compared with 90% for H-Y. In agreement with previous results [12,13,26], H-Y exhibits the highest activity and the highest selectivity in poly-(isopropyl)naphthalenes with the following order: diisopropylnaphthalenes (DIPN) > monoisopropylnaphthalenes (IPN) > triisopropylnaphthalenes (TIPN). The formation of the latter in significant amounts is characteristic of the large extent of multialkylation inside the cavities of H-Y zeolite. On the contrary, H-Mordenite features low activity, but a high selectivity in the monoisopropylation product, 2-isopropylnaphthalene (2-IPN); moreover, among the few polyalkylnaphthalenes formed over H-Mordenite, cyclizates are obtained in larger amounts than the expected classical DIPN.

In the case of H-Beta zeolite, as already pointed out under the introduction section and as shown in Table 2, the formation of cyclizates in significant amounts (cyclizates = IPN = 45–50%) and the low selectivity in DIPN constitute the main features of these results. These cyclizates are also formed over H-Y and H-Mordenite, but in much lesser amount than over H-Beta.

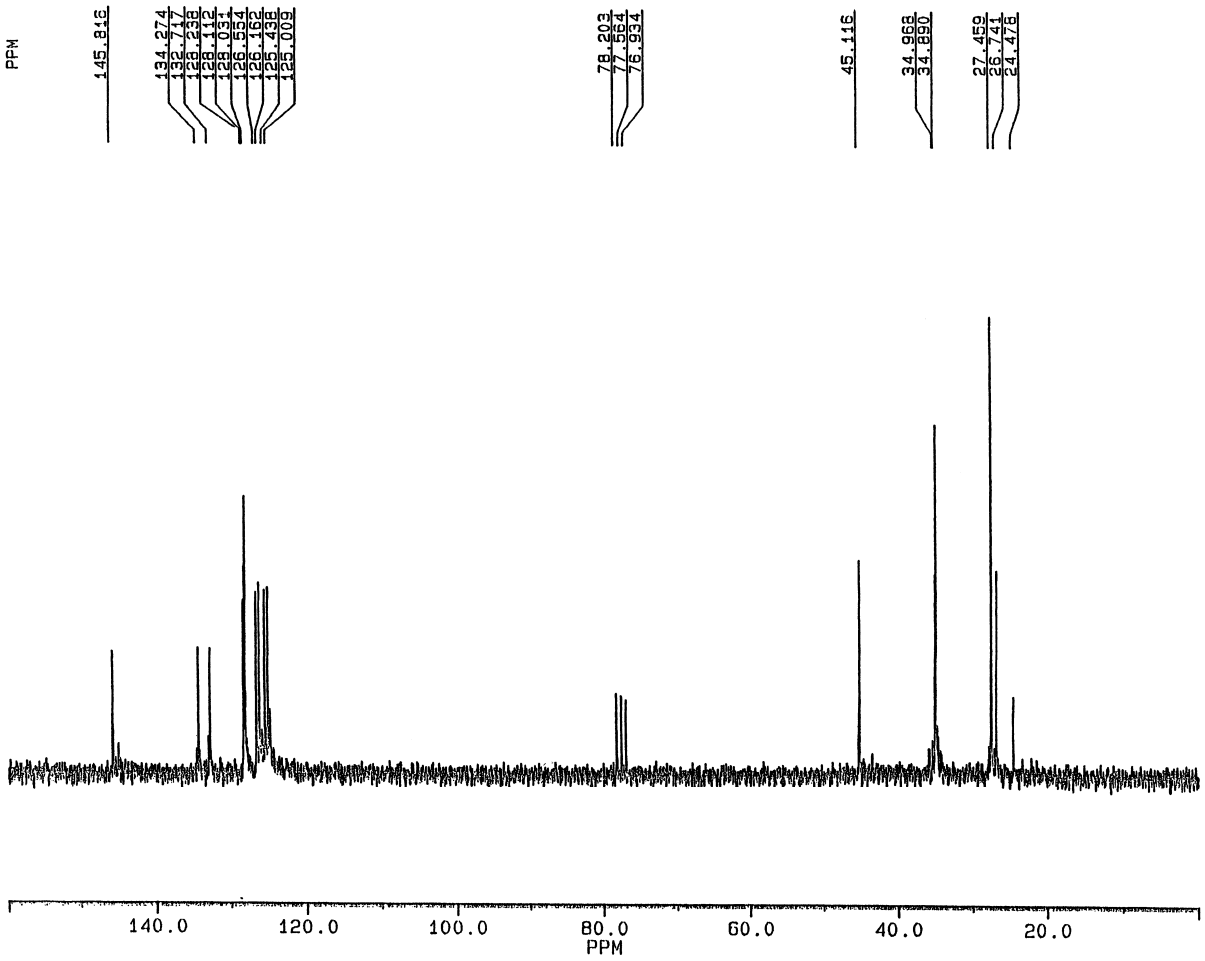


Fig. 2. ^{13}C NMR spectrum of the main "210" isomer.

3.2. Mechanism for the formation of the cyclizates

As a typical aromatic electrophilic substitution reaction, the alkylation of aromatics occurs through the attack of a carbenium ion on the π electrons of the aromatic ring, leading to a σ complex, from which the alkylated derivative is formed with loss of a proton. As for naphthalene, it is known [42] that the α-position is more reactive than the β-position due to a higher electron density, and thus the 1-alkylnaphthalene (α-isomer) is initially formed as the kinetic product. It is then rearranged into the β-isomer (2-alkylnaphthalene) which is thermodynamically more stable. Such a general feature is generally observed in the isopropylation reactions under heterogeneous conditions, whatever the solid catalyst used, in particular zeolites. The β/α ratio (2-IPN/1-IPN) depends on the zeolite type and reaction conditions [8,12,13,26].

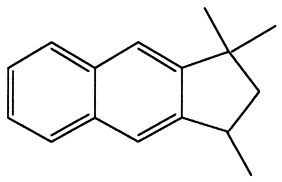


Fig. 3. Structure of the main "210" isomer.

As far as monoalkylation is concerned, the results described above are in agreement with such a feature for the three zeolite samples used in this study. The adsorption of isopropanol on the acid sites of the zeolites leads, by dehydration, to propene via an E1-like mechanism involving C–OH bond breaking and carbenium ion formation. The isopropyl carbenium ion then undergoes an electrophilic attack at the kinetically favorable position, giving 1-IPN, which then isomerizes into 2-IPN under the given reaction conditions.

Over the H-Y zeolite, the formation of the polyisopropyl derivatives, respectively, DIPN (mostly 2,6- and 2,7- isomers) and TIPN, arises from the further alkylation of IPN, according to the same SEAr mechanism (attack of the isopropyl carbenium ion on the monoisopropylnaphthalene), together with some possible secondary isomerization reactions, in agreement with already proposed schemes [7,8,34].

With respect to the formation of the (cyclopentyl)-naphthalene derivatives, it is remarkable to note that

1. over H-Y zeolite, they are not formed until the triisopropylnaphthalenes are obtained, i.e. until three isopropyl groups have been attached to the naphthalene molecule, which leads to the nearly quantitative formation of the “252” cyclizates;
2. over H-Beta and H-Mordenite, on the contrary, they are obtained together with monoisopropylnaphthalenes and at the expense of the diisopropyl derivatives (DIPN), as soon as naphthalene is converted. As indicated in Fig. 4, which shows the evolution of a typical isopropylation reaction over H-Beta versus time, the selectivity in cyclizates increases with reaction time while IPN selectivity decreases; moreover, the “210” cyclizate is the major derivative among the new compounds (more than 80%).

A first hypothesis to explain such results was to assume that over H-Y zeolite, the “252” cyclizate could be formed from the condensation of two isopropyl groups attached to adjacent positions on the same ring of the naphthalene molecule, for example at the 1,2- or 2,3- positions. Such a situation would be favored within the H-Beta and H-Mordenite frameworks. On the contrary, the formation of the “210” cyclizate over H-Beta samples would arise only from a second alkylation of the 2-isopropylnaphthalene. In order to

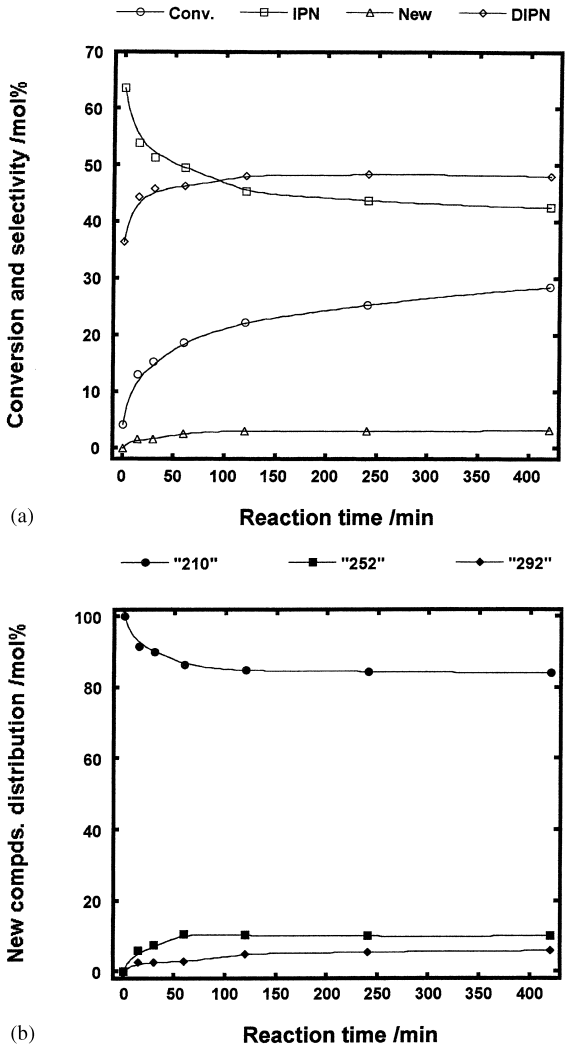


Fig. 4. Typical isopropylation results of naphthalene with isopropanol over H-Beta (12.5) at 473 K. (a) (○) Conversion; selectivities of (◇) new compounds, (□) IPN, and (△) DIPN in products. (b) Distribution in cyclizates with *m/z* (●) “210”, (■) “252”, and (◆) “292”.

verify if the cyclizates could be formed over H-Beta by a similar scheme as that over H-Y, a crude mixture, arising from the isopropylation reaction of naphthalene over H-Y under standard conditions, has been treated over H-Beta in the absence of any alkylating agent. The results obtained from this test, listed in Table 3, first show that the main reaction is concerned with the isomerization of 1-IPN into 2-IPN. Secondly, IPN and DIPN initially produced over H-Y are not

Table 3
Reaction over H-Beta (12.5) of a crude isopropylation mixture obtained over H-Y[a]

Reaction time (min)	Naphthalene content (%)	Product distribution (mol%)							
		1-IPN	2-IPN	DIPN	TIPN	Others	210	252	Total cyclizates[b]
0[c]	32.7	56.2	23.3	16.0	1.9	2.6	0	0	0
20	31.0	43.7	31.1	17.3	4.1	3.8	0	0	0
30	29.8	32.7	42.6	17.7	3.8	3.2	0	0	0
60	29.8	19.0	53.8	17.4	5.7	4.1	0	0	0
120	30.0	12.1	60.7	17.3	4.3	5.2	0	0.4	0.4
240	29.8	9.1	63.8	17.8	5.1	3.7	0	0.5	0.5
420	29.8	6.1	65.4	17.4	5.8	3.9	0.6	0.9	1.5

[a] Reacion conditions: catalyst 0.50 g, cyclohexane 100 ml, 2 MPa; composition of the starting reactant product: isopropylation reaction mixture obtained over H-Y under standard conditions.
[b] "210" + "252".
[c] Composition of the starting reactant mixture.

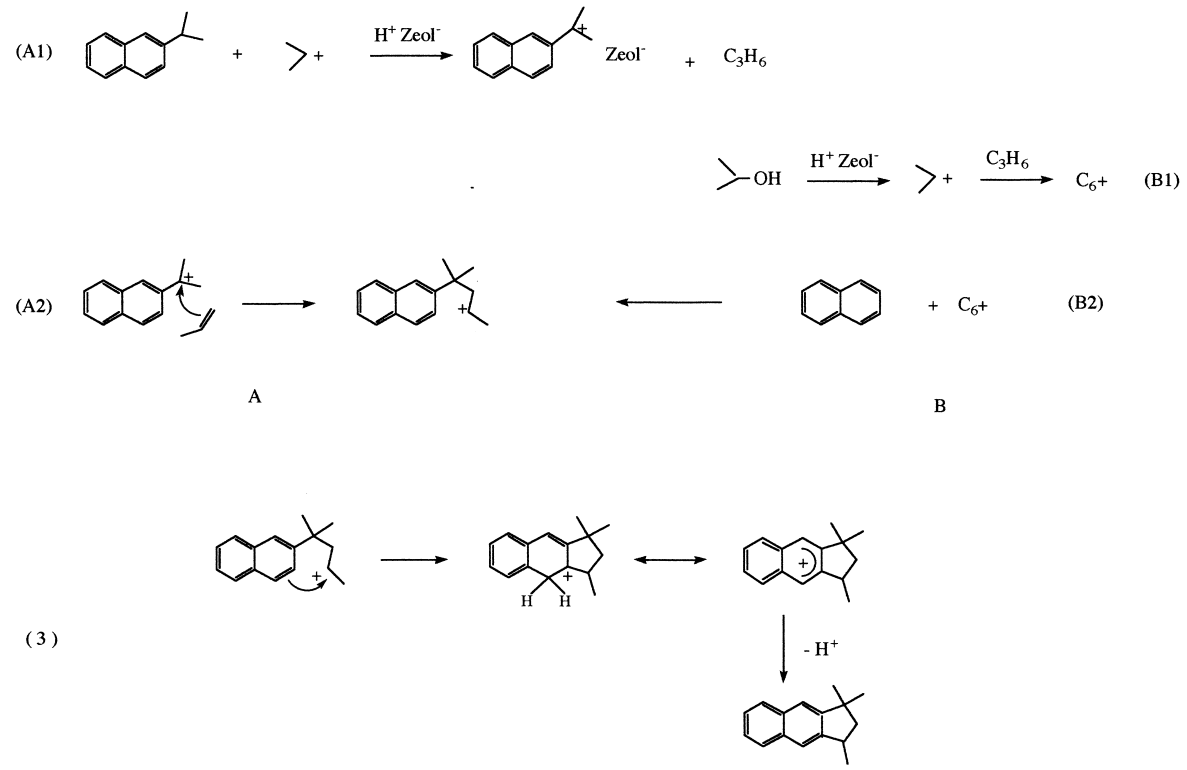
transformed into cyclizates over H-Beta before most of 1-IPN is isomerized into 2-IPN. In particular, no transformation of DIPN (which are mainly a mixture of 2,6- and 2,7- isomers) is observed (their distribution remains nearly constant up to 17% versus time), indicating that cyclizates do not result from 2,6- and 2,7-DIPN isomerization into 1,2- or 2,3- counterparts and further cyclization of the latter.

The data obtained indicate that the differences observed between H-Y on one hand and H-Beta and H-Mordenite on the other hand arise from the further alkylation of the monoisopropylnaphthalene, and must thus be explained by a peculiar orientation of this second alkylation induced by the pore structure of the catalyst.

As already proposed, over H-Y, the further alkylation takes place at an aromatic β′-position, leading to preferential β,β′ dialkylation of the naphthalene molecule. Over H-Beta, such a dialkylation at an aromatic position appears to be not possible, either on the same ring or on the other ring. In order to explain the formation of the "210" cyclizate, one can then invoke an alkane/alkene alkylation type mechanism [43], which would involve the alkylation of the aliphatic chain of the 2-isopropylnaphthalene by a propene molecule.As shown in Scheme 1, the 2-isopropylnaphthalene (2-IPN), once formed, would be strongly chemisorbed on the acid sites of the H-Beta zeolite, leading to a positive isopropylnaphthalenium ion, most likely through hydride transfer from 2-IPN to the existing isopropyl carbenium ion, according to step A1, rather than a protolytic dehydrogenation which could also be assumed to explain the formation of such isopropylnaphthalenium ion. This new isopropyl carbenium ion will then undergo addition to the double bond of a propene molecule formed by dehydration of isopropanol (step A2), to give a new alkyl substituted naphthalenium ion, which easily undergoes a thermodynamically driven cyclization through the attack of the positive charge on the π electrons of the aromatic ring (step 3).

The dehydrogenation of the 2-IPN, leading to the 2-(α-methylvinyl)naphthalene and followed by the attack of the isopropyl carbenium ion onto the double bond could give the same naphthalenium ion, but as the corresponding dehydrogenated naphthalene ($m/e = 168$) is not detected at any time, such a possibility is unlikely.

On the other hand, it is known that oligomers could be formed from propene under certain conditions, especially other H-Y zeolites [34]. Hence, another possible cyclization mechanism could then involve the formation of C6 carbenium ions, generated from reaction of isopropyl carbenium ion with propene (step B1), followed by the SEAr electrophilic attack of one of these carbenium ions on the naphthalene molecule at the 2-position (step B2) and the corresponding cyclization, leading to the "210" cyclizate, according to Scheme 1. Such an alkylation of aromatic ring by a C6 species has been proposed for the liquid-phase isopropylation of benzene to explain the formation of higher alkylbenzenes over H-Beta zeolites [44].



Scheme 1. Possible mechanisms for the formation of cyclizates over H-Beta zeolite.

3.3. Impact of pore structure on product distribution

The lack of formation of cyclizates when a mixture of mono- and diisopropylnaphthalenes is reacted over H-Beta (Table 3) rules out the occurrence of isomerization reactions and multimolecular processes taking place on the isopropylnaphthalene products in their mechanism of formation, and points to a specific orientation of the second addition of an isopropyl group to 2-IPN over H-Beta and H-Mordenite catalysts.

Since the three zeolites feature nearly equivalent composition (Si/Al $= 13 \pm 2$), an argumentation based on a modification of the hard/soft character of the zeolite lattice, as developed by Corma [45,46], seems hardly applicable here, although our data cannot definitively rule out such an alternative. Similarly, *t*-plots derived from the N_2 adsorption/desorption revealed nearly identical mesoporous and external surface areas ($80 \pm 20\,m^2\,g^{-1}$) for the three samples, making improbable some external surface effects.

The most straightforward difference in the three systems investigated here stands, therefore, in the pore architecture of their frameworks, namely the presence of large cavities (13 Å diameter) in H-Y interconnected by 7.4 Å aperture windows, while the porosity of H-Beta and H-Mordenite results only from channels with 6–7 Å pore openings. Indeed, di- and tri-isopropylnaphthalenes can readily be formed in the supercages of H-Y by successive additions of propyl ions to the aromatic ring in IPN. In such an open system, reactants and products can diffuse almost freely in and out the porosity, explaining the high activity and selectivities generally reported with this zeolite and confirmed here.

On the contrary, in the absence of large cavities, alkylation occurs in restricted pores of H-Beta and H-Mordenite in which the motion of the reactants, naphthalene and isopropanol, and of the monoisopropylnaphthalene produced in a first alkylation step may be severely restricted. This is especially the

case of zeolite H-Beta which contains channels with access openings (5.7 Å × 7.5 Å and 6.5 Å × 5.6 Å [36]) that are only slightly larger than the size of naphthalene molecule. Such a situation leads to a much lower activity of the catalysts, and above all, favors unique secondary reactions leading to cyclizates, as exemplified in Scheme 1. It is worth noting that cyclizates were not observed among the alkylation products obtained from benzene and propene, i.e. in the case of a less bulky aromatic substrate, over zeolite H-Beta under a range of experimental conditions [44,47,48]. In addition, cyclizates start to be formed over H-Y when significant amounts of TIPN are produced. Both arguments reinforce the view that the unusual orientation of naphthalene leading to cyclic derivatives results from the steric constraints imposed to the intermediate alkylated products by the rigid framework of zeolite Beta.

4. Conclusion

Liquid phase alkylation of naphthalene with isopropanol has been achieved over large pore H-form zeolites. While H-Y zeolites exhibit the best activity, and show a high selectivity in 2,6- and 2,7-diisopropylnaphthalenes, in agreement with previous studies, the catalytic performance of zeolite H-Beta is somewhat peculiar. Under the same conditions, such a zeolite leads to a series of unexpected compounds, formed in high yields (around 50%), while very little diisopropylnaphthalenes are obtained (less than 5%). H-Mordenites, which feature lower activity, also demonstrate such an unexpected behavior towards formation of multialkylated products. The nature of these compounds has been confirmed, as being (cyclopentyl)naphthalene derivatives (so-called cyclizates). Their formation can be explained by an alkane/alkene alkylation type mechanism, which would involve the alkylation, by a propene molecule, of the side chain of the mono-isopropylnaphthalene, (2-IPN), produced in the first step of the alkylation process, followed by a thermodynamically assured cyclization. Such an unusual process would be favored by the steric constraints imposed on the intermediate alkylated naphthalenics by the rigid channels of zeolite Beta and Mordenite.

Acknowledgements

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