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Selective dialkylation of naphthalene with hindered alkylating agents over HM and HY zeolites under liquid phase conditions

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Abstract

Liquid-phase alkylation of naphthalene with cyclohexyl derivatives as alkylating agents has been studied over HM and HY zeolites. The reaction can be carried out efficiently over HY zeolites, for which high conversions and good selectivities in 2,6- and 2,7-dicyclohexyl naphthalenes (DCN) are obtained after very short reaction times. The ratio 2,6-DCN/2,7-DCN is near to 1, as in the case of the isopropylation reaction over the same catalysts. Such a result is in agreement with the values of critical diameters of 2,6- and 2,7-dicyclohexyl and diisopropyl naphthalenes, calculated by molecular mechanics. The 2,6-dicyclohexyl-naphthalene is a crystalline compound which is easily separated from the reaction mixture by crystallization, which constitutes an interesting advantage of cyclohexylation in comparison with isopropylation.

Keywords: Zeolites; Shape-selective alkylation; Naphthalene; Cyclohexylation; Heterogeneous catalysis

1. Introduction

The alkylation of naphthalene has considerable significance from the point of view of industry. As precursors of 2,6-naphthalene dicarboxylic acid, 2,6-dialkylnaphthalenes are potentially useful raw materials for production of high quality polyester fibers and plastics [1] and of thermotropic liquid crystal polymers [2]. The interest of such derivatives was shown in recent years by the increasing number of patents relevant to their preparation and separation. However, the selective formation of 2,6-dialkylnaphthalenes is not obvious, not only with conventional Friedel-Crafts catalysts [3–5], but also over solid catalysts such as silica-alumina [6–8] or zeolites.

The use of zeolite catalysts had been widely investigated before the beginning of the nineties for the shape-selective conversions of mononuclear aromatic hydrocarbons, such as alkylation of toluene or isomerization of xylenes [9–11].

In contrast, relatively few reports were available on the conversion of polynuclear aromatics, such as naphthalene derivatives, over zeolites. Such solids have been used in the gas phase methylation of naphthalene with methanol [12–14]; large pore zeolites, such as H morden-

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ite or HY, led to a non-selective methylation of naphthalene, whereas a high β-selectivity was observed with the medium-pore H-ZSM-5. Much attention has thus been paid to studies on the activity and selectivity of zeolites in the isopropylation of naphthalene with propene [15,16] or isopropyl bromide [17]. In all cases, a high β-selectivity was found, leading to the selective formation of 2-isopropylnaphthalene and a mixture of 2,6- and 2,7-diisopropylnaphthalenes (DIPN). Over HM catalysts, the preferential formation of 2,6-DIPN among all DIPN isomers has been obtained in the naphthalene alkylation with propene [15,16], and, more recently, with isopropanol [18], with a 2,6-DIPN/2,7-DIPN ratio varying between 2 to 3. In our case, using isopyryl bromide as alkylating agent, we did not observe such a selective formation of the 2,6 isomer, the 2,6-DIPN/2,7-DIPN ratio being around 1. The use of zeolites modified by 'chemical vapor deposition' silanation of the outer surface [19–21], which led to the same results in the distribution of DIPN isomers, allowed us to exclude the possibility of a reaction on the external active sites of the zeolite.

Such different results obtained with the same kind of zeolites (H mordenites) by various authors are not easy to explain and to rationalize, if the molecular dimensions of the 2,6- and 2,7-diisopropylnaphthalenes, which are supposed to be very similar [15,22], are only considered.

On the other hand, good agreements were obtained by the various authors in the results with large pores zeolites such as HY, for which the same distribution between the 2,6- and 2,7-isomers (2,6/2,7-ratio = 1) was found.

We thus considered the use of more hindered alkylating agents, such as cyclohexyl derivatives, in order to improve the selectivity in the 2,6-isomer, taking into account the 2,6-dicyclohexyl naphthalene can be oxidized to 2,6-naphthalene dicarboxylic acid under relatively mild conditions [23].

The present paper is concerned with the comparative study of isopropylation and cyclohexylation reaction of naphthalene over HM and HY zeolites, under liquid-phase conditions.

2. Experimental

2.1. Materials

Analytical grade cyclohexane, cyclohexyl bromide, cyclohexene and naphthalene (Aldrich Chemical) were used as supplied.

2.2. Catalysts

HY (Si/Al = 2.5) is an ultrastable zeolite from Chemische Fabrik Uetikon, Zürich (Z6-05-01). HY (Si/Al = 19.5) and HM (Si/Al = 10.8) are from Zeocat, Montoir de Bretagne (ZF 520 and ZM 510, respectively). Typical properties of these catalysts are shown in Table 1.

2.3. Catalytic runs

For the cyclohexylation of naphthalene with cyclohexyl bromide, the same procedure as that already described for isopropylation [17] was used. When cyclohexene was used, the procedure was the following: the autoclave was charged with naphthalene (5 mmol), cyclohexane (50 ml) and the catalyst (1 g), and heating was started; cyclohexene (10 mmol) was then added, drop by drop, by means of a stainless steel pressurized funnel, and the mixture was stirred.

For the isolation and purification of 2,6-dicyclohexylnaphthalene, the procedure was the

Table 1
Properties of catalysts

Catalyst	Composition (wt%)			Si/Al molar ratio	Specific surface area (m^2 g^{-1})
	SiO_2	Al_2O_3	Na_2O		
HM	92.8	7.2	0.01	10.8	510
HY	74.9	25.1	< 0.2	2.5	675
HY	95.8	4.1	< 0.15	19.5	800

following: after cooling, the catalyst was filtered and cyclohexane evaporated; the crude product which solidified at room temperature was filtered and recrystallized from ethanol (mp 152°C after two recrystallizations). The structure was confirmed by GC-MS, ^{1}H and ^{13}C NMR spectroscopy together with X-ray crystallography [24].

3. Results and discussion

As already discussed in our previous paper [17], mordenites were found to be less active catalysts than Y zeolites in the isopropylation of naphthalene with isopropyl bromide; thus, after 1 h reaction at 200°C, the conversion of naphthalene was 12% over HM (Si/Al = 9.0) and 86% over HY (Si/Al = 2.5).

The maximum conversion of naphthalene (60%) over mordenites was obtained over the Si/Al = 9.0 sample, which is known, in the mordenite series, to correspond to a maximum of activity [25,26]. Moreover, mordenites lead preferentially to the monosubstitution reaction: the major product of the isopropylation reaction was the 2-isopropylnaphthalene not only at low conversion (83% at 12% conversion after 1 h reaction) but also at the maximum of conversion (74% at 60% conversion after 24 h reaction). Such results have already been interpreted in terms of molecular sieve effects due to the constrained environment in the channels of the mordenite [15,17].

The H mordenites present also a very weak activity in the alkylation reaction of naphthalene with cyclohexyl bromide, which has been first chosen as alkylating agent for the cyclohexylation reaction in order to compare with isopropyl bromide. Thus, a 6% conversion of naphthalene was only obtained after 1 reaction at 200°C over an HM (Si/Al = 10.8) sample, whereas HY samples lead to very high conversions (95%) after 10 min reaction under the same conditions.

We thus focused our study of the cyclohexylation reaction by using HY zeolites as catalysts.

Table 2 gives, as an example of the efficiency of Y zeolites, the comparative results obtained over an ultrastable HY zeolite (Si/Al = 2.5) under the same conditions for the reactions with isopropyl bromide and cyclohexyl bromide.

In both cases, a high conversion of naphthalene is obtained as soon as the temperature of 200°C is reached, and the reactions, which both lead to dialkyl naphthalenes as major products, are nearly quantitative after short reaction times (10 min with cyclohexyl bromide, 1 h with isopropyl bromide).

The use of cyclohexyl bromide, instead of isopropyl bromide as alkylating agent, yields an increasing amount of 2,6-+ 2,7-dicyclohexylnaphthalenes (55% instead of 39%), together with a drastically decreasing amount of trialkyl derivatives (2% instead of 17%). This can be attributed to the steric hindrance of the cyclohexyl group compared with isopropyl, and

Table 2
Isopropylation and cyclohexylation of naphthalene over US-HY zeolite at 200°C with isopropyl bromide (IB) and cyclohexyl bromide (CB)

Alkylating agent	Time (min)	Naphthalene conv. (%)	Product distribution (%)						Selectivity (%) 26- + 27-DAN/DAN
				DAN [b]					
			MAN [a]	2,6-	2,7-	2,6- + 2,7-	Others	TAN [c]	
IB	60	97	28	19	20	39	16	17	71
CB	10	96	31	29	26	55	12	2	82

[a] MAN, monoalkylnaphthalenes.

[b] DAN, dialkylnaphthalenes.

[c] TAN, trialkylnaphthalenes.

Table 3
Cyclohexylation of naphthalene over HY(Si/Al = 20) with cyclohexyl bromide (CB) and cyclohexene (CH)

Alkylating agent	T (°C)	Time (min)	Naphthalene conv. (%)	Product distribution (%)			Selectivity (%)		
				MCN	DCN	TCN	2-MCN/MCN	2,6-DCN/DCN	2,6- + 2,7-/DCN
CB	200	10	94	53	46	1	8	43	79
CH [a]	200	10	90	85	15		53	20	36
CH [b]	200	25 [c]	98	44	54	2	7	41	77

[a] CH charged together with naphthalene in the autoclave before heating.
[b] CH added drop by drop.
[c] Time corresponding to the end of addition of naphthalene.

leads to a significant improvement of the β,β-selectivity (82% versus 71%).

In both isopropylation and cyclohexylation reactions, as much of 2,6-isomer is formed as the 2,7-isomer; the relative distribution of the two isomers does not dramatically change (2,6-/2,7-ratio = 0.95 for isopropyl and 1.1 for cyclohexyl). Such a result confirms our previous findings that Y zeolites increase the β,β-selectivity, but do not lead to the predominant formation of one given dialkyl isomer.

The advantage of cyclohexylation in comparison with isopropylation is directly related to the physical properties of the 2,6-dicyclohexylnaphthalene. This compound can be effectively isolated from the reaction mixture by crystallization, as it was reported in earlier studies of the cyclohexylation reaction over aluminum chloride [27,28].

The 2,6-dicyclohexylnaphthalene, a crystalline compound (mp = 152°C) with a crystallographic symmetry centre [24], is thus obtained in a 27% yield from the mixture of the cyclohexylation reaction of naphthalene with cyclohexyl bromide over the ultrastable HY zeolite.

When cyclohexene is used as the alkylating agent instead of cyclohexyl bromide, a slight difference is observed if the reaction is carried out under the same conditions (naphthalene and alkylating agent put together in the autoclave), as shown in Table 3. Such a difference is mainly due to the dimerization of cyclohexene over the acidic sites of the zeolite, dimerization which is known to easily occur for olefins [9,29].

When cyclohexene is added drop by drop, the results are identical to those obtained with cyclohexyl bromide both in conversion and selectivity (Table 3).

This indicates first that the production of hydrogen bromide during the reaction with the bromide reagents does not affect significantly the zeolite catalysts in the reaction times which

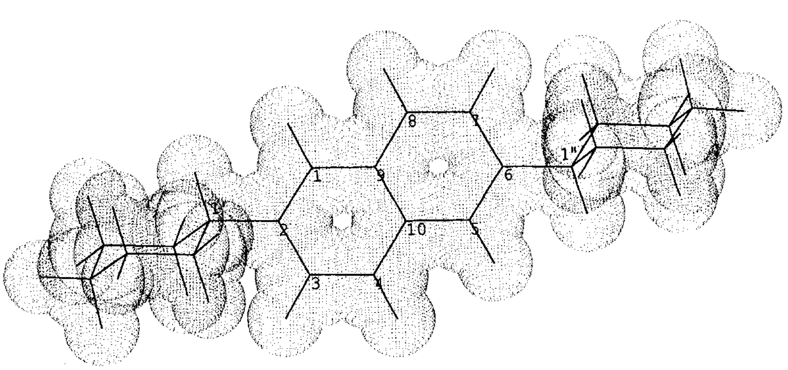

Fig. 1. Molecular graphics of 2,6-dicyclohexyl naphthalene.

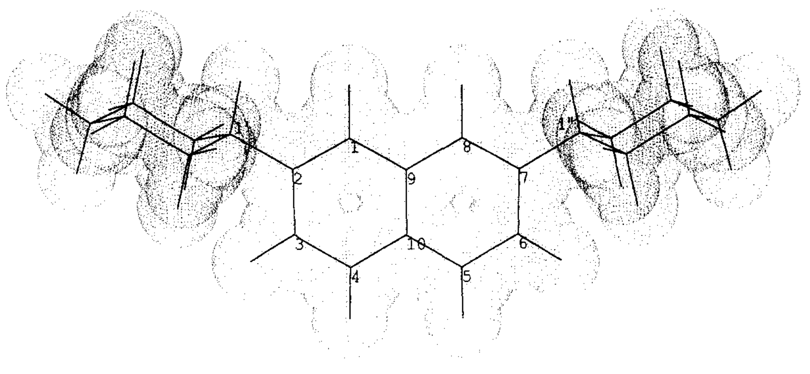

Fig. 2. Molecular graphics of 2,7-dicyclohexyl naphthalene.

are short enough for the quantitative conversion of naphthalene.

Concerning the selectivity, whatever the alkylating agent, cyclohexyl bromide or cyclohexene, the ratio 2,6-DCN/2,7-DCN is near to 1, as in the case of isopropylation. The critical diameters of the two isomers, defined as 'the smallest diameter of a cylinder through which the molecule can pass without distortion' [18], have been calculated on the basis of the intermolecular distances computed by the molecular mechanics method [30]. The software used is 'HyperChem for Windows, release 4.5', with the MM^+ force field module, an enhanced version of the MM2 force field [31], which is very well parametrized for this kind of molecules.

A conformational analysis computed around C_2–C'_1 and C_6–C''_1 or C_7–C''_1 showed that the critical diameters of 2,6-DCN and 2,7-DCN are similar (Figs. 1 and 2).

In fact, the depicted conformations, in which the dihedral angles C_1–C_2–C'_1–H'_1 and C_5–C_6–C''_1–H''_1 or C_8–C_7–C''_1–H''_1 are near to zero degree, are within 0.1 kcal/mol of the lowest energy conformations, and are thus energetically accessible. In these conformations, the calculated critical diameters of 2,6-DCN and 2,7-DCN are 7.1 Å, corresponding to a molecular size of 7.1 × 16.4 Å for the 2,6- and 7.1 × 15.9 Å for the 2,7-, respectively. These calculations are in agreement with the X-ray structure of the crystalline 2,6-DCN [24], which allows us to apply this method to the calculations of critical diameters of the 2,6- and 2,7-diisopropyl analogs (Figs. 3 and 4).

Thus, this method shows that, in the more

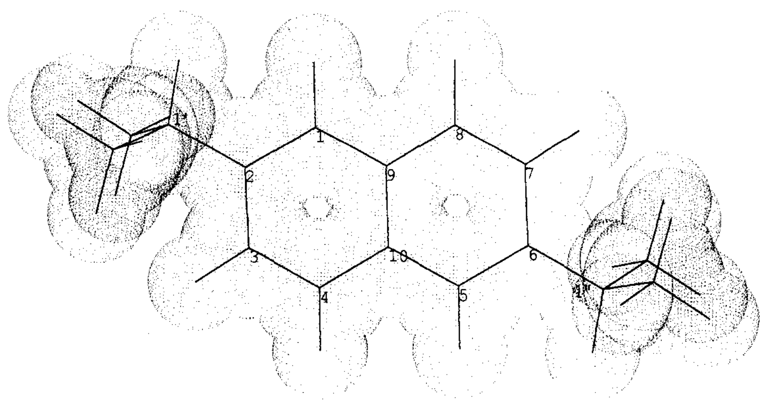

Fig. 3. Molecular graphics of 2,6-diisopropyl naphthalene.

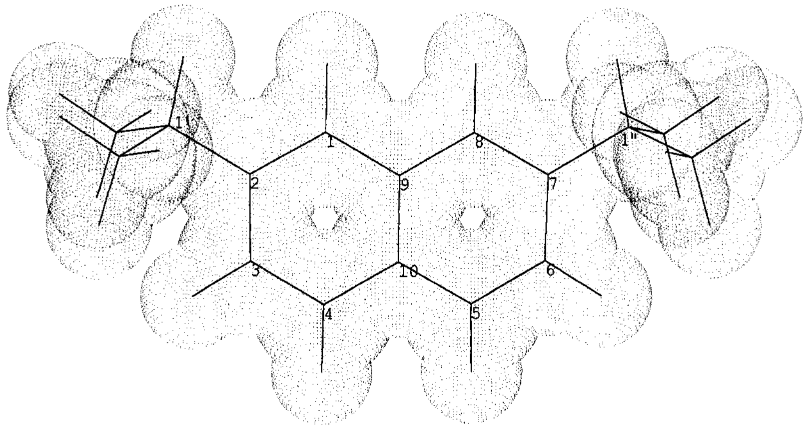

Fig. 4. Molecular graphics of 2,7-diisopropyl naphthalene.

stable conformations (minimum energy), 2,6-DIPN and 2,7-DIPN have the same critical diameters, in accordance with previous authors [15,22]. The corresponding molecular sizes thus calculated are respectively 6.6 × 12.5 Å for the 2,6- and 6.6 × 11.9 Å for the 2,7-isomers.

Such calculations are totally in agreement with our experimental results, not only in the case of Y zeolites, but also in the case of H mordenites with which we obtained a 2,6-DIPN/2,7-DIPN ratio of 1 [17].

4. Conclusion

The liquid-phase alkylation of naphthalene with cyclohexyl derivatives, cyclohexyl bromide or cyclohexene, as alkylating agents, can be carried out efficiently over HY zeolites. High conversions and convenient β,β'-selectivities are obtained after very short reaction times at 200°C. Compared with isopropylation, such a reaction leads to an increasing amount of 2,6- and 2,7-dicyclohexyl naphthalenes (DCN), together with a significant decrease of trialkyl derivatives. Nevertheless, the 2,6-DCN/2,7-DCN ratio is near to 1, as in the case of the already reported isopropylation reaction over the same catalysts. The calculations of the critical diameters by a molecular mechanics method show that these diameters are the same for 2,6- and 2,7-dicyclohexyl isomers (7.1 Å) and for 2,6- and 2,7-diisopropyl (6.6 Å), which is totally in accordance with the experimental results. Moreover, 2,6-dicyclohexyl-naphthalene, a crystalline compound, is easily separated from the reaction mixture by crystallization, which is, to our knowledge, the first example of the production of a pure 2,6-dialkylnaphthalene [32].

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