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Selective Isopropylation of Naphthalene over Zeolites

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The isopropylation of naphthalene with isopropylbromide over a series of H mordenites and Y zeolites has been studied. In both cases, a high β-selectivity is observed in the monoalkylation and dialkylation reactions (selective formation of 2-isopropylnaphthalene and a mixture of 2,6- and 2,7-diisopropylnaphthalenes, respectively). Over H mordenites, the β-selectivity is explained as the result of transition-state shape selectivity. Over Y zeolites, the β-selectivity is due to a thermodynamic equilibrium favorable to the formation of 2-isopropylnaphthalene from 1-isopropylnaphthalene. The use of zeolites modified by silanation using chemical vapor deposition leads to an improvement of the β-selectivity by reducing the amount of trialkyl derivatives that are formed on the external surface. © 1992 Academic Press, Inc.

INTRODUCTION

From the point of view of industry, the alkylation of naphthalene has considerable significance, the most interesting product being 2,6-dialkylnaphthalene, the precursor of 2,6-naphthalene dicarboxylic acid, which is the monomer in the production of polyester fibers with superior properties (*1*).

The alkylation of naphthalene and/or 2-methylnaphthalene with methanol over various zeolites, such as H mordenite (HM), HY, and ZSM-5, has been reported by Fraenkel *et al.* (*2*) and other authors (*3, 4*). A high β-selectivity is observed with ZSM-5 but not with HM and HY. It is postulated that the β-selective methylation over ZSM-5 occurs in external surface sites that perfectly suit small-size naphthalenics.

It is suggested that nonselective alkylation of naphthalene and 2-methylnaphthalene on HM and HY occurs in the intracrystalline voids of these large-pore zeolites that easily accommodate both reactant and product molecules and allow their rapid diffusion.

These results led us to study the isopropylation reaction instead of methylation over various zeolites (HM and Y). The obtainment of 2,6-diisopropylnaphthalene, which is easier to oxidize than 2,6-dimethylnaphthalene, was an interesting first target. Second, because the isopropyl group is more hindered than the methyl group, a β-selective isopropylation could be expected, taking into account that only β-isomers, which have the smallest kinetic diameters (6.5 Å for 2-isopropyl, 2,6-, and 2,7-diisopropylnaphthalenes), would be formed and diffuse into the pores of HM and Y zeolites (pore structure range from 6.7 to 8.0 Å). Moreover, the use of zeolites modified by the "chemical vapor deposition" silanation method (*5*) would be able to enhance such a β-selectivity. It is known that the silanation of zeolites leads to a deactivation of the external sites and also to a uniform control of the pore-opening size of the zeolite (*6–9*). Enhancement of the reactant and product shape selectivity is remarkable with zeolites modified by this method (*10–12*).

The present paper deals with the study of the catalytic "liquid phase" isopropylation of naphthalene (and 2-isopropylnaph-

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thalene) with isopropylbromide as alkylating agent over the above-mentioned zeolites, untreated and modified by octamethylcyclotetrasiloxane deposition. Since the original submission of this paper, Katayama *et al.* (*13*) have reported comparable work concerning isopropylation of naphthalene with propene over zeolites. The results of these authors are discussed together with our own results.

EXPERIMENTAL

(*a*) *Materials*

Analytical grade cyclohexane, isopropylbromide, and naphthalene (Aldrich Company) were used without further purification.

(*b*) *Catalysts*

H mordenite (Zeolon 100-H, Si/Al = 6.9 from Norton) and three mordenites dealuminated following the published procedure (*14*) were used. Dealuminated mordenites were prepared from Zeolon 100-H (HM) by treatment in 1 *M* HCl solution at 100°C for 3 h or refluxing in 3 *M* HCl solution for 6 h or in 6 *M* HCl solution for 12 h. The resulting powders, washed and oven dried at 110°C, had Si/Al atomic ratios of 9 (HM_1), 13.1 (HM_2), and 20.6 (HM_3).

The HY catalyst was derived from thermal decomposition of NH_4Y (Linde SK41, Si/Al = 2.5 from Union Carbide). The CeNaY zeolite was prepared from the parent sodium form (Linde SK40, Si/Al = 2.5 from Union Carbide) by ion exchange following the published procedure (*15*). The US–HY (ultrastable HY) was supplied by Chemisch Fabrik Uetikon (Zürich) (Z6-05-01, Si/Al = 2.6).

(*c*) *Catalytic Runs and Product Analysis*

The isopropylation of naphthalene (or 2-isopropylnaphthalene) was carried out in a 0.1-liter stirred autoclave reactor (Sotelem). In a typical run, the autoclave was charged with 1 g of zeolite freshly calcined in air at 500°C (or 400°C for CeNaY), a mixture of 5×10^{-3} mol of naphthalene or 2-isopropylnaphthalene, and 10^{-2} mol of isopropylbromide in 50 ml of cyclohexane and heated to 200°C. Samples were taken and analyzed by gas–liquid chromatography (Alltech OV1-capillary column 10 m), 100 to 280°C, 10°C/min.

(*d*) *Silanation of Zeolites* (*Chemical Vapour Deposition*)

Three grams of zeolite was calcined in air by heating to 500°C at a rate of 50°C/h and holding the temperature constant at 500°C for 6 h. It was then allowed to cool to 300°C and was used immediately for CVD. The freshly calcined zeolite (2.7 g) was placed in a glass tube of 4 cm in diameter and 15 cm in length with a porous support to allow gas passage through the zeolite. The vessel was heated to 200 or 300°C with an electric furnace. The zeolite was evacuated to 1 Torr for 30 min. In another tube, liquid octamethylcyclotetrasiloxane was kept at 90°C. At time zero, alkoxide vapor was admitted to the dried zeolite, the liquid reservoir being kept open and a continuous vacuum being maintained during deposition. Gaseous compounds passing through the zeolite were condensed at low temperature. Admission of alkoxide vapor was stopped after 6 h and the modified zeolite was evacuated for another 30 min at 200 or 300°C before cooling to room temperature. Materials thus modified were analyzed by microanalysis, and IR spectroscopy of such zeolites will be published separately (*16*).

RESULTS

Experimental results with a series of mordenites and Y zeolites, untreated and CVD modified, are reported in Table 1. From consideration of this table, the following remarks can be made:

(1) Mordenites are less active catalysts than Y zeolites: 24 h are generally necessary to obtain a conversion of 20–30%. Nevertheless, the HM_1 sample, with a Si/Al ratio of 9.0, exhibits a higher activity than the others; it is known, in the mordenite series, that such a ratio corresponds to a maximum

TABLE 1

Isopropylation of Naphthalene over a Series of Untreated and CVD-Modified Zeolites at 200°C

Catalyst	Si/Al	Time (h)	Conv. (%)	Monoalkylnaphthalene	Dialkylnaphthalenes			Trialkylnaphthalenes	2,6- + 2,7-Diisopropyl/ Σ dialkyl	β-Selectivity
				2-Isopropyl	2,6-Diisopropyl	2,7-Diisopropyl	Other dialkyl			
HM	6.9	24	18	81	4	4	3	8	72	89
HM_1	9.0	1	12	83	3	3	2	9	75	87
HM_1	9.0	24	60	74	7	6	5	10	70	87
HM_2	13.1	24	20	61	13	11	9	9	74	85
HM_3	20.6	24	16	55	14	13	7	11	80	82
HY	2.5	0.5	68	68	9	9	7	7	72	85
HY	2.5	1	86	42	16	17	12	14	73	74
US-HY	2.6	1	97	28	19	20	16	17	71	67
CeNaY	2.5	1	73	66	14	14	4	2	87	94
CVD-mod HM	9.5	1	10	90	3	4	3	0	70	97
CVC-mod HY	2.9	1	70	63	15	15	5	2	85	93

of activity (*14*, *17*). On the other hand, the reaction is very fast over Y zeolites (80–90% conversion after 1 h).

(2) The product of monoisopropylation is essentially the 2-isopropylnaphthalene (β-isomer). The α-isomer, the 1-isopropylnaphthalene, is not detected at 200°C in any of the reaction mixtures analyzed. For a given catalyst, as shown in Table 1 for HM_1 and HY, the yield of 2-isopropylnaphthalene decreases and that of 2,6- + 2,7-diisopropylnaphthalenes increases as the conversion increases. Such a result is logically explained by consecutive reactions.

(3) In all cases, 2,6- and 2,7-diisopropylnaphthalenes are the major dialkyl derivatives as shown by the [2,6- and 2,7-diisopropylnaphthalenes]/[total dialkylnaphthalenes] ratio, which is greater than 70% and equal amounts of these two isomers are formed. In the case of mordenites, the other dialkylnaphthalenes are essentially ethylisopropylnaphthalenes formed by a partial dealkylation of 2,6- and 2,7-diisopropylnaphthalenes. In the case of the Y zeolites, these dialkyl derivatives are a mixture of the latter ethylisopropylnaphthalenes and of three diisopropylnaphthalenes other than the 2,6- and 2,7-isomers.

(4) The β-selectivity corresponds to the [2-isopropyl + (2,6 + 2,7)-diisopropylnaphthalenes]/[total product] ratio. In all cases, the β-selectivity is suitable, 67% minimum.

(5) Over both mordenites and Y zeolites, trialkyl derivatives are formed in substantial amounts (HM, 8–11%; HY, 14–17%).

(6) Among the Y zeolites studied, the most active is the ultrastable sample US–HY; nevertheless, as a consequence of stronger acidic sites (*18*, *19*), the amount of trialkyl derivatives is increased, so that the β-selectivity is lower.

(7) The Y zeolite exchanged with Ce^{3+} cations leads to an interesting product distribution: the main products are the 2-isopropylnaphthalene (66%) and the 2,6- and 2,7-diisopropyl isomers (28%), with only 2% of trialkyl derivatives. Such a result, which leads to a very high β-selectivity (94%), can be the consequence of a fast deactivation of the catalyst.

(8) Over CVD-modified zeolites, conversions are lower, as expected; for example, 70% instead of 86% in the case of HY after 1 h. Consequently, the formation of polysubstituted products is reduced.

DISCUSSION

(*a*) *Conversion*

The mordenites are generally known to be more acidic than Y zeolites, and this is especially true for the HM_1 (Si/Al = 9.0) compared with the HY (Si/Al = 2.5) (*14*, *20*, *21*).

In our study, mordenites are less active than Y zeolites as shown in Table 1; thus, the conversion of naphthalene, after 1 h reaction at 200°C, is 12% over HM_I and 86% over HY. Such a result is explained by the particularly straight channel structure of mordenites, in which the diffusion of reactants and products is slower than in the three-dimensional channels of the faujasite type zeolites.

(*b*) *Monoisopropylation Reaction*

It was seen that, at 200°C, no 1-isopropyl naphthalene was detected whatever the zeolite used. When the isopropylation reaction is run at lower temperature, 80°C, the results are different depending on the catalyst:

(i) over HM, no 1-isopropylnaphthalene is detected,

(ii) over HY, the two isomers are observed.

Such results can be explained as follows. In the case of H mordenites, the steric hindrance of the α-isomer (kinetic diameter 8.1 Å) does not allow its formation inside the tight one-dimensional (6.7 × 7.0 Å) tunnels of the zeolite. In the three-dimensional large-pore (7.5 Å) Y zeolites, on the other hand, the 1-isopropylnaphthalene can be formed. It is known that the α-position of naphthalene is more reactive than the β-position (*22*), so that the α-isomer is initially formed (kinetic product). It is then rearranged into the β-isomer, which is thermodynamically more stable (thermodynamic product). Such a rearrangement is very fast at 200°C, which explains that only the 2-isopropylnaphthalene is obtained at high temperatures.

However, despite the molecular size of the 1-isopropylnaphthalene being slightly higher than the pore aperture of the Y zeolites, its formation and its diffusion are allowed, because of the flexibility of guest molecules; this leads to deviations from the expected shape selectivity (*2*). Consequently, the origin of the β-selectivity observed in the isopropylation reaction of naphthalene depends upon the structure of the zeolite.

Over H mordenites, the alkylation in the more reactive α-position is impossible, so that it takes place only in the β-position leading to the 2-isopropyl derivative with a smaller conversion. Such results are consistent with those of Katayama *et al.* (*13*) and are characteristic of a molecular sieve effect, due to the constrained environment in the channels of the mordenite, leading to a transition-state shape selectivity.

Over Y zeolites, the β-selectivity is due to a thermodynamic effect that favors the 2-isopropylnaphthalene at high temperatures (equilibrium $\alpha \rightleftharpoons \beta$ 1.5–98.5 (*23, 24*)), and consequently, in a second consecutive step, the formation of the $\beta\beta'$-disubstituted isomers (2,6- and $-\lambda$2,7-diisopropylnaphthalenes).

(*c*) *Diisopropylation Reaction*

As previously stated, 2,6- and 2,7-diisopropylnaphthalenes are the main disubstituted derivatives over the two kinds of zeolites. Such a result is expected, taking into account the β-selectivity observed in the monoisopropylation step, whatever the origin of this selectivity.

Over Y zeolites, in accordance with the report of Katayama *et al.* (*13*), as much of the 2,6-isomer is formed as the 2,7-isomer. Over mordenites, the same distribution of these two isomers is obtained, contrary to the results reported by Katayama *et al.* (*13*) and Fellmann *et al.* in a recently published patent (*25*) who obtain 2,6/2,7 ratios of 2 and 3, respectively. This is surprising since these two isomers have the same kinetic diameter (6.5 Å) and their production and subsequent diffusion in the pores or cavities of zeolites occur in the same way, as confirmed by our own results. Other reasons must be put forward to explain the fact that the 2,6-isomer is formed in a bigger proportion than the 2,7: these reasons are not given by the different authors (*13, 25*).

(*d*) *Use of CVD-Modified Zeolites*

It is clear that the trialkyl compounds derived from the $\beta\beta'$-isomer cannot be formed inside the lattice of the mordenite because of their kinetic diameters (8.1 Å). It is assumed that the trialkylation reaction occurs on catalytic acid centers located on the zeolite external surface.

As shown in Table 1, the production of the bulky trialkyl is totally suppressed over a CVD-modified HM zeolite. As previously stated, the CVD silanation technique leads to a deactivation of the external surface (*6–9*) confirming that the external sites are responsible for the formation of the trisubstituted derivatives.

The same CVD technique was applied to the HY zeolite. In that case, the formation of the trialkyl derivatives is considerably reduced, but not totally suppressed. The remaining 2% (compared with 14% over the untreated zeolite) may be formed inside the large-pore Y zeolite, invoking the same phenomenon as mentioned above for the 1-isopropylnaphthalene.

Similar results are obtained in the isopropylation of the 2-isopropylnaphthalene over CVD-modified HY zeolite, i.e., a reduced conversion (54% instead of 73% over the untreated HY) and a drastic decrease in the amount of trialkylnaphthalenes (4% instead of 18% over the untreated HY), leading to an enhancement of the β-selectivity over this CVD-modified HY (85% instead of 74%).

The overall results show that, from a synthetic point of view, the CVD-modified zeolites appear to be the best catalysts with which to selectively obtain β- and $\beta\beta'$-isomers.

With CVD-modified HM, the 2-isopropylnaphthalene is the major product (90% at 10% conversion). Despite the low conversion, this result must be taken into account because 2-isopropylnaphthalene can be easily separated from the reaction mixture by simple distillation, and then isopropylated as starting material for diisopropylnaphthalene production. Also, unreacted naphthalene can be recycled for new reactions.

With CVD-modified HY zeolites, a high β-selectivity is obtained, corresponding to 63% of 2-isopropylnaphthalene and 30% of 2,6- + 2,7-diisopropylnaphthalenes at 70% conversion (it is worth mentioning that the Y zeolite exchanged with Ce^{3+} cations gives the same results).

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