

Unusual results in the liquid phase alkylation of naphthalene with isopropyl alcohol over zeolite H-beta

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Unexpected compounds are formed with high selectivity in the liquid phase alkylation of naphthalene with isopropyl alcohol over large pore zeolite H-beta; these have been confirmed to be cyclized products from naphthalene derivatives.

2,6-Dialkyl-naphthalenes are valuable compounds for the production of high-quality polyester fibres, plastics and thermotropic liquid crystal polymers.¹ Taking into account that these compounds are manufactured inefficiently by the nonselective alkylation of naphthalene over conventional Friedel–Crafts catalysts² or solid silica–alumina catalysts,³ considerable attention has recently been paid to the development of new processes for the selective preparation of 2,6-dialkyl-naphthalenes using environment-friendly zeolite catalysts. Owing to the steric hindrance of naphthalene, medium pore zeolites, such as HZSM-5, show moderate activity in naphthalene alkylation.^{4,5} Large pore zeolites, such as Mordenite, beta, Y, and more recently mesoporous aluminosilicates, have been investigated. Alkylating agents bulkier than MeOH, such as isopropyl^{5–9} or cyclohexyl derivatives^{7,10} and butanol,^{11,12} have been also applied successfully to the selective formation of 2,6-dialkyl-naphthalenes. Among these studies, substantial advances have been made in naphthalene isopropylation for both the understanding of the alkylation mechanism and the design of catalysts leading to high selectivity in forming 2,6-diisopropyl-naphthalenes.^{5–9} H-beta has been shown to be more active and selective than HY in the alkylation of benzene with propylene¹³ but did not demonstrate selectivity in the alkylation of polyaromatics until recently.^{5,9,11,12} Nevertheless, it has been reported that H-beta shows an unexpected high selectivity for *sec*-butylbenzene in the alkylation of benzene with isobutyl alcohol.¹⁴ In our search for suitable catalysts for the selective synthesis of 2,6-dialkyl-naphthalenes, we have recently found another peculiar characteristic of H-beta zeolite in the liquid phase alkylation of naphthalene with isopropyl alcohol, in which a series of unexpected compounds were formed with high yield under given conditions. Here we report on the unusual results thus obtained and the identification of the new compounds.

Zeolite catalyst H-beta (Si/Al = 12.5) was obtained from PQ Corporation (CP 810 B-25). HY (Si/Al = 15) was prepared by

standard ion-exchange, calcination, steam dealumination and acid leaching procedures from a parent synthetic zeolite. Activation of H forms was achieved by calcination at 773 K for 5 h with a heating rate of 60 K h⁻¹ in a flow of dry air. The isopropylation of naphthalene was carried out in a 0.16 dm³ stirred autoclave reactor (Parr Instrument Company). Under standard reaction conditions, 10 mmol of naphthalene, 20 mmol of PrⁱOH, 10 mmol of undecane as an internal standard sample and 0.1 dm³ of cyclohexane as solvent were mixed together in the autoclave, and then freshly calcined zeolite (0.5 g) was added. The reaction temperature was set at 473 K and the pressure was maintained at 2 MPa with nitrogen. Samples were withdrawn periodically and analysed on a Varian Series 30 gas chromatography equipped with HP-5 capillary column (25 m) and a FID detector. GC–MS (HP5970) with an OV1 capillary column (25 m) and NMR (Brücker AC200) analysis were used for the identification of the new compounds.

Typical reaction results are listed in Table 1. The activity of H-beta is much lower than that of HY, as shown by the naphthalene conversion which reaches a maximum of 30% under standard reaction conditions, compared with 90% for HY. GC–MS analysis indicates that the new compounds have molecular mass (*m/z*) of 210, 252 and 292, respectively, different from the products usually obtained in naphthalene isopropylation over large pore zeolite catalysts^{5–9} which are isopropyl-naphthalene (IPN), diisopropyl-naphthalene (DIPN), triisopropyl-naphthalene (TIPN) and tetraisopropyl-naphthalene (TetiPN) with molecular mass of 170, 212, 254 and 296, respectively. As shown in Table 1, H-beta possesses a peculiar catalytic function for the production of the new compounds. After 2 h, the selectivity (around 50 mol%) of total new compounds is higher than that of alkylated derivatives, mainly IPN (43 mol%). DIPN selectivity is unexpectedly low and no TIPN is detected. Such a result is totally different from those obtained by Chu and Chen⁵ who used continuous fixed-bed reactor conditions. In agreement with previous results, HY zeolite shows a higher activity and selectivity for DIPN and TIPN than H-beta. It is observed that the new compounds are also formed over HY, but in much smaller amounts than over H-beta. Moreover, the distribution of the new compounds produced over the two zeolites are different. H-beta gives more than 80 mol% of '210' and less '252' or '292', while HY

Table 1 Reaction results of isopropylation of naphthalene over different zeolites at 473 K^a

Catalyst	<i>t</i> /h	Conv. (%)	Product distribution (mol%)					New compound distribution (mol%)			
			IPN	DIPN	TIPN	New	Others ^b	'210'	'252'	'292'	'294'
H-beta	1	18.7	49.6	2.6	0	46.3	1.5	86.2	10.8	2.8	0.0
	7	28.5	42.6	3.1	0	48.1	6.2	84.0	10.2	6.0	0.0
HY	1	92.3	36.9	41.1	14.7	5.9	1.4	0.0	88.9	0.0	11.1
	7	94.6	31.1	46.2	14.2	7.1	1.4	0.0	91.7	0.0	8.3

^a Reactions conditions: catalyst (0.5g), naphthalene (10 mmol), PrⁱOH (20 mmol), undecane (10 mmol), cyclohexane (100 ml), 2.0 MPa. ^b Others include methyl(isopropyl)naphthalene and ethyl(isopropyl)naphthalene

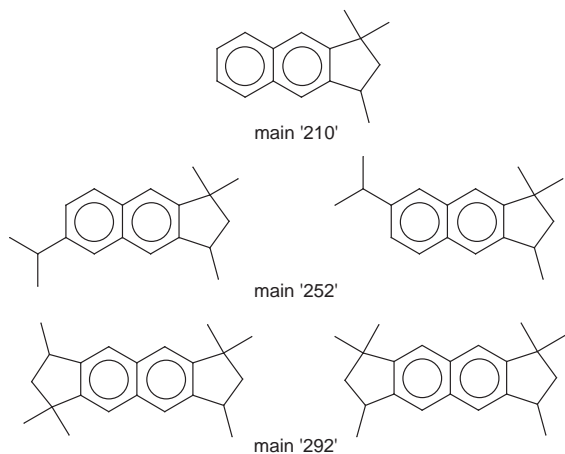


Fig. 1 Proposed structures for the main isomers in new compounds

produces mainly '252' and almost no '210'. There were also many isomers among the new compounds. In fact, there were at least five isomers of '210' and seven isomers of '252' and '292'.

The identification of these new compounds has been made possible by GC-MS and ^{13}C NMR analysis. First, a simple conclusion can be drawn from GC-MS results. Products '210' and '252' could be derived from DIPN and TIPN respectively by removing H_2 , and '292' could be produced from TetIPN by removing two equiv. of H_2 , suggesting that in a '210' molecule, for example, a branched double bond or an additional hydrocarbon ring might be formed. Second, no dehydrogenated derivative (e.g. m/z 168) from IPN (m/z 170) is detected, implying that dehydrogenation takes place only between two isopropyl groups, resulting in the cyclization. Therefore, the new compounds are most likely the cyclized products from DIPN, TIPN and TetIPN. That is, one or two additional rings have been formed on naphthalene in the reaction process.

A mixture of the new compounds was isolated by distillation from the products of naphthalene isopropylation over H-beta with the following composition: 79 mol% of '210' (which contains 72% of the main '210' isomer), 9.5 mol% of '252' and 10.6 mol% of '292'. ^{13}C NMR measurements have been applied to this mixture and the obtained spectrum has been compared to those of methyl styrene, indane and tetralin, selected as possible comparable samples, and those of related compounds such as benzocyclobutane, octamethylcyclobutane and dimethylcyclobutanes.¹⁵ The characteristic signals near δ 145.8 in the ^{13}C NMR spectrum of this enriched mixture are similar to those of benzocyclobutane (δ 145.2)¹⁵ or indane (δ 144.3), possibly due to the quaternary carbon atoms of a four- or five-membered ring fused to a benzene ring. This signal position is different in tetralin, where the chemical shift of the corresponding quaternary carbon is at δ 137.4. Therefore, the new additional ring cannot be six-membered. Moreover, the two other signals near δ 45.1 given by the enriched mixture are similar to those obtained with octamethylcyclobutane or 1,1-dimethylcyclopentane for the corresponding quaternary carbon atom.¹⁵ Accordingly, the new ring formed on naphthalene might be five- or four-member. Furthermore, the GC analysis of the products of naphthalene isopropylation over H-beta indicates

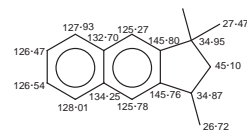


Fig. 2 ^{13}C NMR chemical shifts of the main '210' isomer

that there is one main isomer (72%) among the five '210' species and two main isomers (>90%) among the seven '252' and '292' species. Such a distribution suggests that the new ring formed in naphthalene is a five-member ring substituted by methyl groups at positions 2',2' and 4', which is the only structure able to give one '210' and two '252' isomers.

Thus, according to the mass, ^{13}C NMR and GC analyses of the new compounds, the structures of the main isomers of '210', '252' and '292' might be consistent with those depicted in Fig. 1, minor isomers possibly resulting from methyl migration and/or ring contraction. The assignment of the ^{13}C NMR chemical shifts of the main '210' isomer (as an example) is indicated in Fig. 2.

Further studies are in progress to elucidate the mechanism and driving force leading to the formation of the new compounds.

The authors thank the France-China PICS-program (No.299) for financial support.

Notes and References

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Received in Cambridge, UK, 15th June 1998; 8/045081