Shape-selective alkylation of 2-methoxynaphthalene with *tert*-butanol over large-pore zeolites

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The selective formation of 6-*tert*-butyl-2-methoxynaphthalene is reported for the first time in the liquid phase alkylation of 2-methoxynaphthalene with *tert*-butanol over large-pore zeolites (maximum of 96% selectivity over H-MOR at 65% conversion). Over H-Y, which has been shown to be the most efficient catalyst in such a reaction in terms of activity, the main secondary reactions are the dialkylation, leading to bulky di-*tert*-butyl-2-methoxynaphthalene derivatives, and the demethylation of the methoxy group, giving mono- and di-*tert*-butyl derivatives of naphthol.

KEY WORDS: alkylation; 2-methoxynaphthalene; *tert*-butanol; zeolites; heterogeneous catalysis; Naproxen.

1. Introduction

Friedel–Crafts alkylation and acylation are useful steps for creating a C–C bond in organic synthesis [1]. Alkylation is one of the most important steps in the petrochemical and fine chemicals industry. In general, Lewis metal halides like $AlCl_3$, $FeCl_3$, $TiCl_4$ and $SnCl_4$ are used as catalysts for aromatic alkylation, but the use of these conventional catalysts leads to a number of disadvantages [2,3]. They are non-regenerable, more than a stoichiometric amount of the catalyst is needed, a tedious work-up procedure is required, and formation of hazardous side products like halogenated organics leads to environmental problems; moreover, the use of such catalysts suffers from selectivity problems.

Most of the above drawbacks can be overcome by using easily recoverable and regenerable solid acid catalysts like zeolites. During the past three decades, zeolite catalysis has proved to be a useful supplementary technology in both the petrochemical industry and the manufacture of fine chemicals and chemical intermediates [4–8], and the advantages of such zeolites are now well demonstrated [9]. Zeolites have been especially extensively studied for the alkylation of mononuclear aromatic hydrocarbons, and proved to be promising solids for achieving highly shape-selective catalysis [10,11]. Due to the demand for the corresponding symmetrically substituted dialkyl derivatives, the use of medium- and large-pore-size zeolites in the alkylation of polynuclear aromatics, such as naphthalene and biphenyl, has also drawn the attention of different groups [12–14]. Such reactions have been more recently developed, and large-pore zeolites, such as

H-MOR, H-Y and H-BEA, have been found to be efficient catalysts for the selective synthesis of 2,6-dialkylnaphthalenes [15–20] and 4,4′-dialkylbiphenyls [21–24]. On the other hand, a number of papers have recently appeared concerning the use of large-pore zeolites, especially H-Y and H-BEA [25–36], and of mesoporous molecular sieves [37] in the acetylation reaction of 2-methoxynaphthalene. The main objective of the latter studies was to develop active solid catalysts for the selective formation of 2-acetyl-6-methoxynaphthalene, a precursor to the anti-inflammatory drug Naproxen [38]. The alkylation of 2-methoxynaphthalene could be an alternative route to produce other precursors of Naproxen, and the use of titanium- and zirconium-containing molecular sieves in the alkylation of 2-methoxynaphthalene with propylene oxide has been recently reported [39,40].

In the continuation of our previous works on the alkylation of polynuclear aromatics under liquid-phase heterogeneous conditions, the present paper deals with the results obtained in the alkylation of 2-methoxynaphthalene with *tert*-butanol over large-pore zeolites as acid catalysts, leading to efficient conversions of 2-methoxynaphthalene and very high selectivities in the desired 6-*tert*-butyl-2-methoxynaphthalene. The effect of temperature on the main and secondary reactions has been especially investigated.

2. Experimental

2.1. Catalyst materials

The catalysts H-Y (Si/Al = 15, CBV 720) and H-MOR (Si/Al = 10, CBV 20A) were obtained from the

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Catalyst	Si/Al ratio	Pore structure (nm)	S_{BET} ($m^2 g^{-1}$)	Acidity (NH_3-TPD) (mmol $H^+ g^{-1}$)
H-MOR	10	0.65×0.70, 0.26×0.57	403	1.30
H-MOR	45	0.65×0.70, 0.26×0.57	468	0.38
H-Y	15	0.74×0.74	697	0.56
H-BEA	12.5	0.55×0.55, 0.76×0.64	681	1.03

PQ Corporation; H-BEA (Si/Al = 12.5, CP 814E) was obtained from Zeolyst Int. The characteristics of the various samples are given in table 1. The calcination of the catalyst was carried out in the presence of air at 500 °C for 6 h with a ramping rate of 60 °C h^{-1}.

Analytical grade *tert*-butanol, naphthalene (Aldrich Company) and cyclohexane were used without further purification.

2.2. Catalytic runs

The reactions were carried out in 0.16 l stirred autoclave reactor (Parr Instrument Company). In a typical run, 2-methoxy naphthalene (1.58 g, 10 mmol), *tert*-butanol (1.48 g, 20 mmol) and 100 ml of cyclohexane as solvent were mixed together homogeneously in the autoclave, and 0.5 g of zeolite, freshly calcined and kept at 200 °C in a flow of dry air, was added. Then the autoclave was sealed and flushed with N$_2$ several times in order to replace the air. The temperature was set according to the reaction experiments. Zero time was taken when the desired temperature was reached. The conversion was calculated on the basis of 2-methoxynaphthalene converted.

2.3. Product analysis

The samples were withdrawn periodically from the autoclave and analyzed by using a Girdel chromatograph equipped with an OV-1 capillary column (25 m) and FID detector. The analysis program was 70 °C to 250 °C at a ramping rate of 15 °C min^{-1}, and 250 °C maintained for 10 min isothermally.

The products *tert*-butyl-2-methoxynaphthalenes (TBMN), *tert*-butyl-2-naphthols (TBN), di-*tert*-butyl-2-methoxynaphthalenes (DTBMN), di-*tert*-butyl-2-naphthols (DTBN) and 2-naphthol were identified by GC-MS (Hewlett-Packard Model 5890, coupled with an MS-5970A mass spectrometer and a 2671G data system) analysis. The main products 6-*tert*-butyl-2-methoxynaphthalene (2,6-TBMN) (II) and 6-*tert*-butyl-2-naphthol (6-TBN) (IV) were isolated from the final crude product obtained from the reaction over H-MOR catalyst

after 24 h, under standard conditions, through silica gel column chromatography using cyclohexane/ethyl acetate as eluent. Further purity was confirmed by GC, and the structure confirmed by ^{1}H and ^{13}C NMR spectroscopy.

Physicochemical characterization of the products
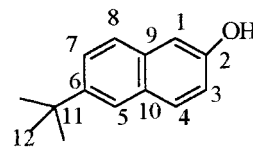
6-*tert*-butyl-2-methoxynaphthalene (II)
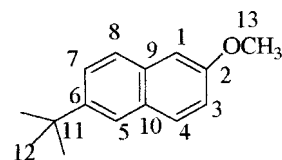
NMR

^{1}H: ppm: 1.5–1.6 (9H, s), 3.9–4.0 (3H, s), 7.2–7.7 (4H, aromatic)
^{13}C: ppm: 105.5 (C1), 157.33 (C2), 118.5 (C3), 129.4 (C4), 125.2 (C5), 146.29 (C6), 122.7 (C7), 126.5 (C8), 132.68 (C9), 128.9 (C10), 34.66 (C11), 31.37 (C12), 55.3 (C13).
MS: *m/z* (%): 214 (25), 215 (5), 199 (100), 200 (16), 184 (7), 171 (16), 158 (11), 152 (9), 141 (10), 139 (10), 128 (14), 115 (15), 99 (5), 85 (10), 76 (5), 63 (5), 41 (6).

6-*tert*-butyl-2-naphthol (IV)

NMR

^{1}H: ppm: 1.45–1.5 (9H, s), 7.2–7.7 (4H, aromatic), (H, hydroxy)
^{13}C: ppm: 109.14 (C1), 153.0 (C2), 117.58 (C3), 129.28 (C4), 122.7 (C5), 146.28 (C6), 122.6 (C7), 125.5 (C8),132.7 (C9), 128.9 (C10), 34.65 (C11), 31.3 (C12).
MS: *m/z* (%): 200 (29), 201 (3), 185 (100), 186 (17), 169 (5), 171 (5), 152 (5), 144 (17), 139 (5), 127 (11), 115 (19), 93 (8), 84 (8), 78 (16), 66 (9), 51 (9), 41 (11).

3. Results and discussion

3.1. Effect of catalyst type

Typical reaction results for the different zeolite catalysts used in the alkylation of 2-methoxynaphthalene with *tert*-butanol under standard conditions are listed in table 2.

The three samples H-Y, H-BEA and H-MOR, with a similar Si/Al ratio (10 to 15), exhibit high initial activity (50% for H-MOR and H-BEA and more than 65% for H-Y within 30 min reaction). Moreover, a nearly quantitative conversion (99.1%) of 2-methoxynaphthalene

Table 2
tert-Butylation of 2-methoxynaphthalene with *tert*-butanol over different zeolite catalysts at 160 °C

Catalyst	Time (h)	Conversion of 2-MN (mol%)	Distribution of products (%)					
			II	III	ΣTBMN	ΣTBN	ΣDTBMN	ΣDTBN
HY (15)	0.5	65.9	90.9	1.8	92.7	1.4	4.4	1.5
	2	79.4	85.0	1.2	86.2	4.8	6.3	1.7
	6	99.1	72.0	1.3	73.3	13.7	9.7	3.3
H-BEA (12.5)	0.5	50.2	100.0	–	100.0	–	–	–
	2	58.8	94.0	–	94.0	3.0	3.0	–
	6	64.2	81.1	–	81.1	7.2	4.1	–
H-MOR (10)	0.5	50.6	100.0	–	100.0	–	–	–
	2	65.0	96.0	–	96.0	2.6	1.4	–
	6	73.0	91.6	–	91.6	7.3	1.1	–
H-MOR (45)	0.5	18.3	100.0	–	100.0	–	–	–
	2	23.6	100.0	–	100.0	–	–	–
	6	35.9	93.4	–	93.4	6.6	–	–

Note: Reaction conditions: catalyst, 0.5 g; *tert*-butanol, 20 mmol; 2-methoxynaphthalene, 10 mmol; solvent, cyclohexane 100 ml.

is obtained after 6 h reaction over H-Y, whereas the conversion is nearly constant after 2–4 h over H-MOR and H-BEA, indicating deactivation of the catalyst to a certain extent. Nevertheless, convenient conversions are achieved over the latter catalysts, 73% and 64% respectively. In the absence of any zeolite, under the same conditions, no conversion is observed after 6 h reaction.

The activity of the different samples stands in the order H-Y (15) ≫ H-MOR (10) > H-BEA (12.5). This order is the reverse of the total acidity of these catalysts, measured by NH₃–TPD, which is H-MOR > H-BEA > H-Y (table 1). As already shown in other electrophilic aromatic substitution reactions [41], the higher activity of H-Y is undoubtedly related to the large-pore tri-dimensional zeolite network and the presence of supercages, which allows the reaction to occur onto the hindered substrate within the framework without diffusional restrictions.

Scheme 1 shows the plausible reaction pathways for the formation of these products. The primary products, the mono-alkylated isomers (II) and (III), especially compound (II), are predominant; they further undergo dialkylation to form (VI) and a dealkylation (demethylation) reaction to form mono-alkylated derivatives of 2-naphthol, (IV) and (V). By demethylation of the methoxy group, (VI) leads to the formation of (di-*tert*-butylnaphthols) (VII), while (IV) and (V) are able to undergo a dealkylation reaction to form 2-naphthol (VIII) in small amounts.

Concerning the distribution of the reaction products, it is interesting to point out a significant selectivity in the monoalkylation step, whatever the catalyst, especially in the case of H-MOR for which a maximum of 96% selectivity in compound (II) is obtained at 65% conversion after 2 h reaction. Moreover, for both H-MOR and H-BEA, the 6-*tert*-butyl-2-methoxynaphthalene (II) is the only product of monoalkylation, while, over H-Y, small amounts (1.3%) of other mono-*tert*-butylated isomer (III) are obtained at maximum conversion.
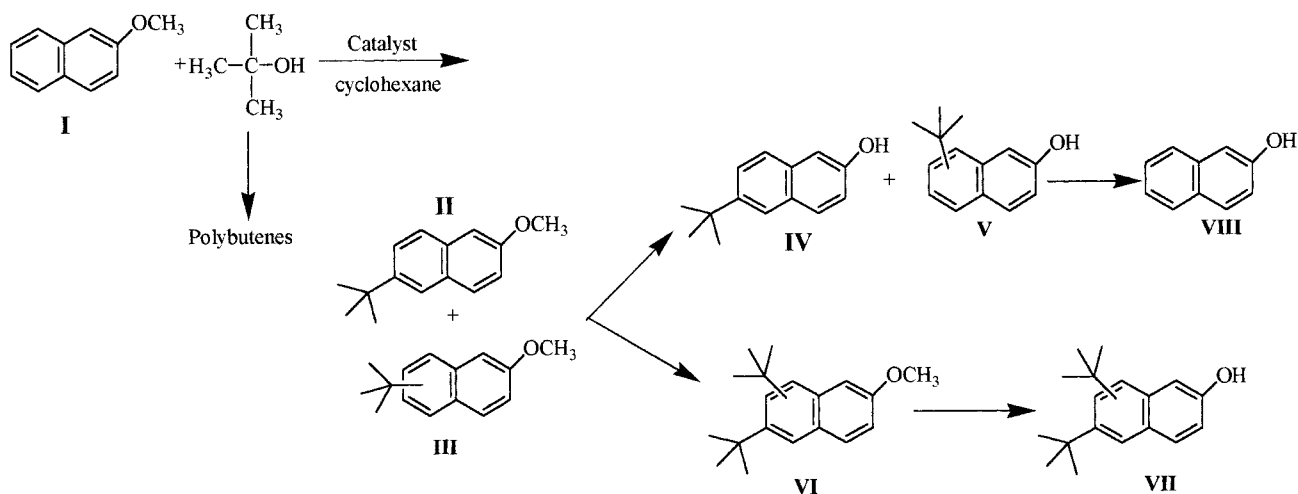
Scheme 1. Reaction pathways for *tert*-butylation reaction of 2-methoxynaphthalene with *tert*-butanol over zeolite catalysts.
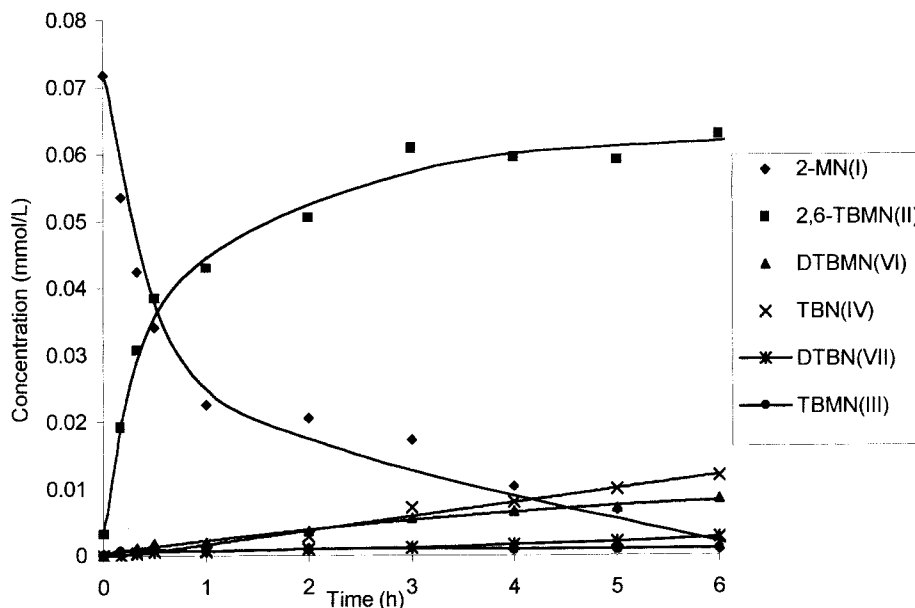
Figure 1. *tert*-Butylation of 2-methoxynaphthalene over H-Y catalyst at 160 °C: consumption of 2-methoxynaphthalene and formation of products *versus* time.

Finally, it can be seen from table 2 that the conversion of 2-MN is lower when the reaction is carried out with a dealuminated H-MOR (Si/Al = 45) compared with the more acidic (Si/Al = 10); the conversions after 30 min (18.3% over H-Y (45) and 50.6% over H-Y (10)) are in good agreement with the total acidities of these samples (table 1) which are respectively 0.38 and 1.30. Such a result means that all the catalytic sites are efficient in the reaction.

It is known that, in naphthalene series, an electron-donating group like OCH_3 at the 2-position activates the electrophilic substitution at the 1-, 6- and 8-positions of the naphthalene ring. The 1-position of 2-MN is the most reactive, and undesired 1,2-alkylated derivatives are generally obtained under classical Friedel–Crafts conditions [42]. Although the 1-position is the most reactive, the steric hindrance developed by the bulky *tert*-butyl group at this position prevents the formation of the corresponding 1,2-isomer within the framework of most of the large-pore zeolites used. The alkylation at the 6-position is thus favored, leading to the sterically less hindered and linear product. The predominant formation of the 2,6-isomer, compound (II), over the H-Y zeolite and its selective formation over H-MOR and H-BEA can thus be easily explained by the shape selectivity nature of these microporous solids, in connection with the size of the molecules: the kinetic diameters, determined by using the method of the "smallest box enclosing solute" function of Hyperchem software [43] are 6.8 Å for the 6-*tert*-butyl-2-methoxynaphthalene (II), but higher than 8.0 Å for the more hindered isomers (III). This computational method allows measurement of the dimensions of the molecules in their minimum energy configuration in three-dimensional space [44]; after

minimization of the energy, the kinetic diameter of the molecule is determined using the width of the closest box enclosing the molecular system [45], the van der Waals radius of hydrogen 1.1 Å and a conversion factor $2^{-1/6}$ [46]. Such a feature is confirmed by the fact that the further alkylation of (II) (and to some extent of (III)) leading to bulky di-*tert*-butyl-2-methoxynaphthalene derivatives (ΣDTBMN), for which the values of the kinetic diameters measured as above are 8.3 to 8.8 Å, is mainly observed in the case of the tri-dimensional and supercage framework of the H-Y zeolite.

The consumption of 2-methoxynaphthalene and the formation of the various products *versus* time over the H-Y catalyst at 160 °C are presented in figure 1.

This figure first shows that, at the initial time t_0, the measured concentration of 2-methoxynaphthalene is 0.072 (instead of 0.1) while only very few products are formed; such a feature is characteristic of a strong adsorption of the substrate onto the catalyst. On the other hand, the increase in the dialkylated-2MN (ΣDTBMN, (VI), 9.7% after 6 h) is accompanied by the increase of *tert*-butylnaphthols ((IV), (V), 13.7% after 6 h), together with corresponding di-*tert*-butyl-naphthols (VII, 3.3% after 6 h), arising from the demethylation reaction of the methoxy group of the corresponding dialkylated ethers.

It is worth mentioning that, in the case of H-MOR samples, the di-*tert*-butyl derivatives are formed in very small amounts, but that *tert*-butylnaphthols arising from the demethylation reaction [44] are formed in some extent (7.3% at 73% conversion for H-MOR (10) and 6.6% at 35.9% conversion for H-MOR (45)) (table 2). Such a result can be explained by the fact that the

Table 3
tert-Butylation of 2-methoxynaphthalene over H-Y catalyst: effect of temperature on activity and selectivity

Temperature (°C)	Time (h)	Conversion of 2-MN (mol%)	Distribution of products (%)					
			II	III	ΣTBMN	ΣTBN	ΣDTBMN	ΣDTBN
110	0.5	39.0	100	–	100	–	–	–
	2	49.0	97.0	–	97.0	–	3.0	–
	6	59.0	93.8	2.4	96.2	–	3.3	0.5
130	0.5	47.3	91.5	2.8	94.3	0.5	4.2	1.0
	2	61.0	90.2	2.7	92.9	0.8	4.5	1.2
	6	74.0	87.9	2.3	90.2	1.3	5.5	1.8
160	0.5	65.9	90.9	1.8	92.7	1.4	4.4	1.5
	2	79.4	85.0	1.2	86.2	4.8	6.3	1.7
	6	99.1	72.0	1.3	73.3	13.7	9.7	3.3
200	0.5	74.9	90.3	–	90.3	5.0	4.7	–
	2	79.0	87.7	–	87.7	7.6	4.7	–
	6	75.3	88.0	–	88.0	7.7	4.3	–

Note: Reaction conditions: catalyst, 0.5 g; *tert*-butanol, 20 mmol; 2-methoxynaphthalene, 10 mmol; solvent, cyclohexane 100 ml.

demethylation reaction is catalyzed by the acid sites of both H-MOR samples, but preferentially by strong acid sites, which is the case of the more dealuminated H-MOR (45). Moreover, the unidimensional structure of the H-MOR allows and facilitates the dealkylation reaction at the expense of the dialkylation (leading to sterically hindered derivatives), unlike the tridimensional framework of the H-Y catalyst.

Moreover, when the reaction is carried out in the absence of *tert*-butanol (*i.e.* only with 2-methoxynaphthalene) no dealkylated or any other isomerized products are observed over H-Y and H-M catalysts, whereas, when the same reaction, in the absence of *tert*-butanol, is carried out from a mixture of 2-methoxynaphthalene and 6-*tert*-butyl-2-methoxynaphthalene over H-Y, only the 6-*tert*-butyl-2-naphthol is obtained. These results show that the *tert*-butyl naphthols (IV and V) are obtained from the demethylation of *tert*-butyl-2-methoxynaphthalenes (II and III), and not by the *tert*-butylation of naphthol. Naphthol formation is then due to the further dealkylation of *tert*-butyl naphthol and not to the demethylation of 2-methoxynaphthalene; the demethylation is favored by the inductive donating effect of the *tert*-butyl group.

It has been shown that, under these conditions (160 °C), an excess of *tert*-butanol (*tert*-BuOH/2-MN = 3 or 5) did not affect the conversion of 2-methoxynaphthalene, which was nearly quantitative (99%) after 6 h reaction whatever the excess; such an excess of *tert*-butanol just led to a logical increase of the di-*tert*-butyl derivatives (13.1% *versus* 9.7% at 99% conversion under standard conditions). On the contrary, at a *tert*-BuOH/2-MN of 1, the conversion of 2-MN was lower (80%), and the main secondary reaction was the demethylation reaction, leading to 15.2% of *tert*-butyl-2-naphthol (IV); only very small amounts (3%) of dialkyl derivatives were logically obtained in that case.

3.2 Effect of temperature

Table 3 shows the influence of reaction temperature on both activity and selectivity in the alkylation of 2-methoxynaphthalene with *tert*-butanol over the most active catalyst H-Y (Si/Al = 15) under standard reaction conditions. From this table, it can be seen first that significant conversions can be obtained even at a low temperature such as 110 °C (nearly 60% after 6 h reaction). At such a temperature, the main reaction is the monoalkylation (97% selectivity in the 6-*tert*-butyl-2-methoxynaphthalene (II) at 49% conversion); moreover, the only secondary reaction is the further alkylation of (II) leading to the corresponding di-*tert*-butyl derivative (VI) in very small amounts (3% at 49% conversion). No demethylation, *i.e.* no formation of naphthol derivatives, is observed at this temperature.

An increase of the temperature from 110 to 160 °C leads to a significant, but logical, effect on the conversion of 2-methoxynaphthalene with a nearly quantitative conversion (99%) obtained at 160 °C after 6 h reaction. This increase of the conversion is accompanied by a corresponding decrease of the selectivity of the monoalkylation step (73.3% of (II) + (III) at 99% conversion). Concerning the secondary products, it is important to point out that, at 130 °C, the main secondary reaction is dialkylation (5.5% of di-*tert*-butyl derivatives (VI) + (VII) at maximum conversion), whereas, at 160 °C, the demethylation reaction of the methoxy group, leading to the *tert*-butylnaphthols (IV) + (V) and di-*tert*-butylnaphthols (VIII) (respectively 13.7 and 3.3% at 99% conversion) is significantly more important than the dialkylation (9.7% at the same conversion). Such a result is the reverse of that obtained at 110 °C (see above), which indicates that the dealkylation reaction requires a higher activation energy than the dialkylation step to occur. This is in agreement with the results obtained with the H-MOR samples; in that

case, the demethylation reaction is catalyzed by the strong acid sites of the dealuminated H-MOR (45), and not by the weaker acid sites of the H-MOR (10). The demethylation is a strong condition demanding reaction (strong acidity or high temperatures are required).

The same trend (demethylation more important than dialkylation) is observed at 200 °C. At this temperature, it is surprising to note that the maximum conversion (75–80%) is lower than that obtained at 160 °C; this is certainly due to the fact that, at such a high temperature, *tert*-butanol is consumed by the formation of polybutene oligomers, such as dimer and trimer, which suppress the further alkylation of 2-methoxynaphthalene by lack of the alkylating agent.

4. Conclusions

The liquid phase alkylation of 2-methoxynaphthalene with *tert*-butanol has been investigated over large-pore zeolites, such as H-Y, H-BEA and H-MOR, with the objective to obtain a possible intermediate for the synthesis of Naproxen. H-Y has been shown to be an efficient catalyst in such a reaction, allowing a nearly quantitative conversion of 2-methoxynaphthalene after a short reaction time under mild conditions. In all the cases, a very high selectivity in the desired product, the 6-*tert*-butyl-2-methoxynaphthalene, has been achieved; over H-Y, the main secondary reactions have been shown to be the dialkylation, leading to bulky di-*tert*-butyl-2-methoxy-naphthalene derivatives, and the demethylation of the methoxy group, giving mono- and di-*tert*-butyl derivatives of naphthol. The relative distribution of these products depends mainly on the temperature of the reaction, but also on the structure of the catalyst; it has been especially shown that the unidimensional structure of the H-MOR allows and facilitates the demethylation reaction of the methoxy group at the expense of the dialkylation (leading to sterically hindered derivatives), unlike the tridimensional framework of the H-Y catalyst. A maximum of 96% selectivity for the 6-*tert*-butyl-2-methoxynaphthalene was obtained over H-MOR (10) at 65% conversion.

Acknowledgments

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