

Selective alkylation of biphenyl over H-MOR and H-BEA zeolites: analysis of experimental results by computational modelling

Jana Horniakova^a, Dusan Mravec^{a,1}, Jacques Joffre^b, Patrice Moreau^{b,*}

^a Department of Organic Technology, Faculty of Chemical and Food Technology, Slovak University of Technology, 812 37 Bratislava, Radlinskeho 9, Slovak Republic

^b Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, UMR 5618 CNRS, ENSCM, 8 rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France

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Abstract

Computational analysis of molecular dimensions and diffusion parameters of the various mono- and diisopropyl and *tert*-butylbiphenyl isomers within H-MOR and H-BEA zeolite framework has been performed using molecular mechanics and quantum mechanics methods. The calculated values have been compared with the experimental results obtained in the isopropylation and *tert*-butylation reactions of biphenyl with the corresponding alcohols over these large pore zeolites as catalysts. The calculated results are in good agreement with the experimental results achieved in the *tert*-butylation of biphenyl over H-MOR and H-BEA zeolites. The 4-MTBB and 4,4'-DTBB having a kinetic diameter of 5.8 Å and the smallest energy barriers are formed preferentially over both zeolites. In the case of the isopropylation reaction, the experimental results achieved over H-MOR are in a good agreement with the computational analysis, whereas over H-BEA, where the more hindered 3-MIPB and 3,4'-DIPB are preferentially formed despite of their higher kinetic diameters and energy barriers, the experimental results are somewhat different from the computational ones. The differences are related to the special architecture of BEA zeolite which allows the diffusion of relatively hindered molecules through its pores, contrary to the uni-dimensional structure of MOR zeolite. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Shape-selective catalysis occurs by differentiating reactants, products and/or reaction intermediates according to their shape and size. The catalytic alkylation of polynuclear aromatics, such as biphenyl and naph-

thalene, using suitable shape-selective zeolites constitutes one of the best examples of the achievement of such a shape-selectivity.

The linear 4,4'-dialkylated biphenyls and 2,6-dialkylated naphthalenes are important intermediates for the preparation of special types of polyesters [1,2]. In recent years, a great attention has been devoted to the isopropylation of biphenyl and naphthalene [3–7] with propylene or isopropanol as alkylating agents. Dealuminated and cerium modified H-mordenites have especially been found to be efficient catalysts for the selective isopropylation of biphenyl [8–13].

* Corresponding author. Tel.: +33-4-6714-4325; fax: +33-4-6714-4349.

E-mail addresses: mravec@chtf.stuba.sk (D. Mravec), pmoreau@cit.enscm.fr (P. Moreau).

¹ Tel.: +421-2-59-32-53-27; fax: +421-2-52-49-31-98.

As for us, we recently studied the selectivity of large pore zeolites, such as H-Y and H-beta, in the alkylation of naphthalene [14,15] and biphenyl [16,17] with *tert*-butanol. We also showed that dealuminated H-mordenites displayed high selectivities in both mono- and di-alkylation in the *tert*-butylation of biphenyl [18].

Computational modelling has been shown to be an efficient method of screening possible catalysts for shape-selective reactions. Catalytic conversion of molecules in zeolites is influenced by several factors, among which the relative diffusion rates of reactants and products could play an important role. The information about interactions at the molecular level is difficult to obtain experimentally. The diffusion energy profiles calculated from interaction energies appear to be very useful and elegant to derive the diffusion energy barriers for possible products of a studied reaction, moreover they indicate relative diffusion rates of molecules in the zeolite framework. A molecular graphic screening of potential catalysts for the selective synthesis of 2,6-diisopropyl-naphthalene inside mordenite channel has been first reported by Horsley et al. [19] by using molecular mechanics force field. More recently, Vetrivel and coworkers [20–23] have reported several studies based on the calculations of diffusional parameters for various molecules and different zeolites and especially they used molecular graphics to analyse the efficiency of large pore zeolites in the synthesis of 4,4'-diisopropylbiphenyl (DIPB) [20].

On the other hand, Song et al. [24], on the basis of computational analysis using MOPAC program, confirmed that the formation and diffusion of 2,6-diisopropyl-naphthalene inside mordenite channel was easier than that of 2,7-isomer. In our case, we have performed a computational analysis of both energies and molecular dimensions of mono- and di-*tert*-butyl-naphthalenes, which allowed us to understand the significant difference in the alkylation of naphthalene with *tert*-butanol over H-Y zeolites obtained for the formation of 2,6- and 2,7-di-*tert*-butyl-naphthalenes [15].

More recently, we have reported the computational analysis of the selective isopropylation of biphenyl over H-mordenites [25]. The results indicate that the desired product, the 4,4'-DIPB, has the lowest kinetic diameter and diffusion energy inside the mordenite

channel compared with the other DIPB isomers. The calculated results were in agreement with the experimental results regarding the high *para*- and *para,para'*-selectivities observed in the isopropylation of biphenyl.

The present work is focused on the calculation and comparison of diffusional parameters for possible products of biphenyl *tert*-butylation and isopropylation with alcohols (*tert*-butanol and isopropanol) as alkylating agents inside the channels of BEA and MOR zeolites to find an explanation at the molecular level for a different behaviour of these zeolites in the studied reactions.

2. Experimental

Zeolites H-MOR (17.5) (CBV 30 A) and H-BEA (12.5) (CP 814 E) from PQ were used as catalysts for *tert*-butylation and isopropylation of biphenyl in the liquid phase. Characteristics of these zeolites, activation to the catalytic form, experimental procedure (catalytic runs) and product analysis have been already described in previous papers [16,18].

3. Methodologies and results

3.1. Molecular dimensions

The molecular dimensions of studied molecules were calculated using the *smallest box enclosing solute* function of Hyperchem 6.0 [26]. Beforehand and in order to find the best conformation of each molecule, potential energy surfaces and Monte-Carlo conformational analysis were computed. Among the computational methods for the determination of energies available in Hyperchem, the AMBER force field and the semi-empirical quantum AM1 hamiltonian were chosen, because such methods give optimized geometries close to the experimental ones, particularly for the dihedral angle of the biphenyl molecule [27].

After minimization of the energy, the kinetic (or critical) diameter of the molecules was determined using the width of the closest box enclosing the molecular system [21], the van der Waals radius of hydrogen is 1.1 Å and the conversion factor is $2^{-1/6}$ [28]. The values of kinetic diameters thus obtained

for *tert*-butylbiphenyl and isopropylbiphenyl isomers will be discussed later on.

3.2. Diffusion energies

The diffusion energies of the molecules inside zeolite channel were computed using the minimum energy profile technique described by Horsley et al. [19]. The MOR and BEA zeolite channels were modelled according their crystallographic structure [29], with SiO clusters ($\text{Si}_{140}\text{O}_{213}$ for a MOR cluster 52 Å long and $\text{Si}_{168}\text{O}_{252}$ for a BEA cluster 72.7 Å long). It must be pointed out that, for these calculations, an ideal channel of the zeolite is used; additional factors, such as the chemical composition of the zeolite framework and the acidic properties of the zeolite together with the mechanism of the formation of the products (primary or secondary) are not taken into account. The sorbate molecule was forced to diffuse in regular steps of 0.2 Å within the channel. At each point, the geometry of the biphenyl derivatives was optimized by determination of the energetically favourable conformation and position by varying their internal degrees of freedom, whereas the atoms in the zeolite lattice were kept constant at their crystallographically determined geometries. This process allowed to draw a diffusion energy profile which shows the variation in the interaction energy between the molecule and the zeolite framework as the molecule diffuses within the channel. Such profiles have been obtained by using AMBER calculation method, in which the van der Waals energies are only taken into account as non-bonded interactions. Thus, diffusional characteristics of studied molecules in the zeolite channel such as diffusional energy barrier, the mean energy and diffusivity can be derived from obtained diffusional

profiles. Diffusional energy barrier is defined as the difference of energy at the most favourable (minimum energy) and the most unfavourable (maximum energy) adsorption sites inside the zeolite channel. The mean energy is the numerical average of the interaction energy of the molecule at all locations. The ratio of mean energy/minimum energy indicates the diffusivity of molecule as defined by Vetrivel and coworkers [22,23].

3.2.1. Zeolite MOR

Mordenite has an orthorhombic symmetry and pore structure is uni-dimensional (1D) [29]; an elliptical 12-MR channel ($7.0 \times 6.5 \text{ \AA}^2$) runs along the [00 1] direction with small pockets (4.8 Å, 8-MR) along [0 1 0] direction. The energy parameters calculated from the diffusion energy profiles of possible isopropylbiphenyl and *tert*-butylbiphenyl isomers in the mordenite channel are listed in Table 1.

Concerning the mono-*tert*-butylbiphenyl (MTBB) derivatives, the minimum energy profiles of considered 3-MTBB and 4-MTBB isomers show a higher energy barrier for 3-MTBB (4.3 kcal/mol) in comparison with 4-MTBB isomer (3.8 kcal/mol). Thus, the diffusion of 3-MTBB should be slower than 4-MTBB. The energy barriers calculated from energy profiles for di-*tert*-butylbiphenyl (DTBB) isomers are also in the same order (1.1 kcal/mol for 4,4'-DTBB, 17.2 kcal/mol for 3,4'-DTBB, 31.2 kcal/mol for 3,3'-DTBB, respectively). Moreover, the diffusivity, defined as above [18], of considered molecules decreases in the order 4, 4'-DTBB > 4-MTBB > 3, 4'-DTBB > 3-MTBB \gg 3, 3'-DTBB. The energy diffusional profiles drawn for 4,4'- and 3,3'-DTBB are presented in Figs. 1 and 2, respectively, as typical examples.

Similar results are obtained for isopropylbiphenyl isomers; 4-MIPB (mono-isopropylbiphenyl) has the

Table 1

Energy parameters calculated from diffusion energy profiles for various isomers in the isopropylation and *tert*-butylation of biphenyl in mordenite zeolite

Molecule	Isopropylation			<i>tert</i> -Butylation		
	Barrier (kcal/mol)	Mean energy (kcal/mol)	Diffusivity	Barrier (kcal/mol)	Mean energy (kcal/mol)	Diffusivity
3-Alkyl	3.6	−21.6	0.86	4.3	−18.9	0.74
4-Alkyl	2.2	−26.0	0.96	3.8	−25.8	0.92
3,3'-Dialkyl	7.1	−32.9	0.90	31.2	−17.4	0.58
3,4'-Dialkyl	6.8	−32.8	0.91	17.2	−21.1	0.79
4,4'-Dialkyl	1.7	−37.9	0.96	1.1	−32.0	0.98

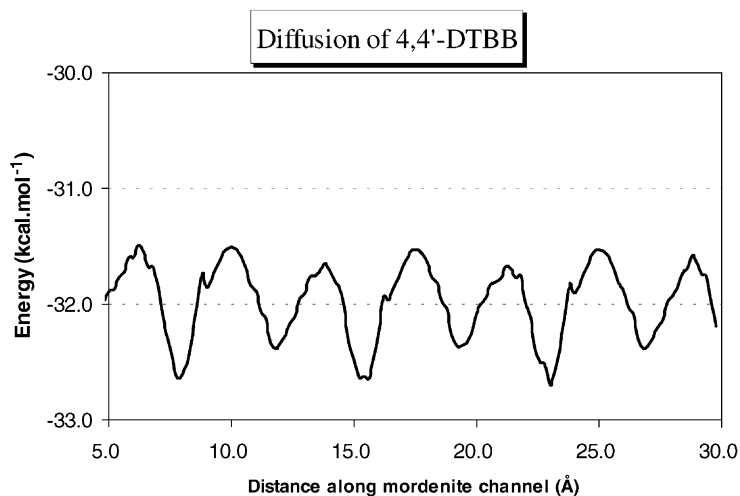


Fig. 1. Energy profile for the diffusion of 4,4'-DTBB in mordenite.

smallest energy barrier (2.2 kcal/mol) among MIPBs and 4,4'-DIPB (1.7 kcal/mol) among diisopropylated derivatives. In the same way, the diffusivity of the molecules stands in the order 4,4'-DIPB = 4-MIPB > 3,4'-DIPB > 3,3'-DIPB > 3-MIPB.

3.2.2. Zeolite BEA

BEA has a three-dimensional interconnected (3D) channel system with 12-membered ring openings. In-

terconnected linear pores with an opening of $7.7 \times 6.6 \text{ \AA}^2$ run in [1 0 0] and [0 1 0] directions, and communicate through perpendicular connecting openings of $5.6 \times 5.6 \text{ \AA}^2$ in the [0 0 1] direction [29,30].

The energy parameters calculated from the diffusion energy profiles for isopropylated and *tert*-butylated biphenyls in BEA channel are listed in Table 2, and the diffusion energy profiles of, respectively, the 4,4'-DIPB, 4,4'- and 3,3'-DTBB are presented in Figs. 3–5.

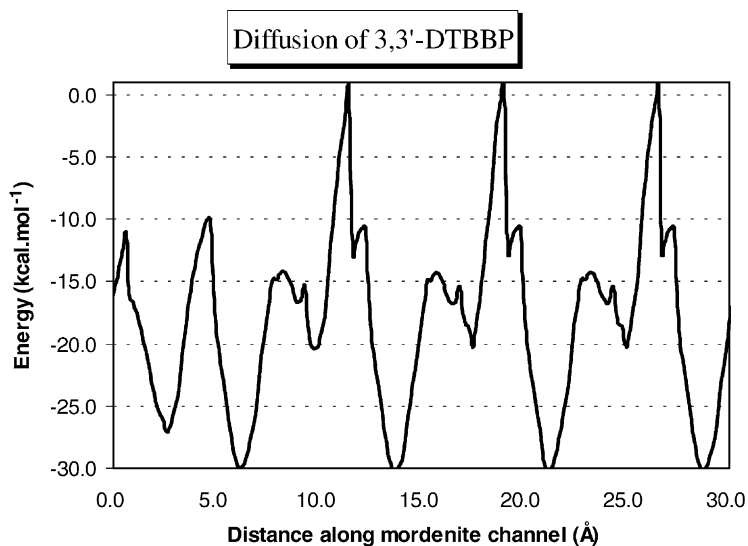


Fig. 2. Energy profile for the diffusion of 3,3'-DTBB in mordenite.

Table 2

Energy parameters calculated from diffusion energy profiles for various isomers in the isopropylation and *tert*-butylation of biphenyl in BEA zeolite

Molecule	Isopropylation			<i>tert</i> -Butylation		
	Barrier (kcal/mol)	Mean energy (kcal/mol)	Diffusivity	Barrier (kcal/mol)	Mean energy (kcal/mol)	Diffusivity
3-Alkyl	4.3	−17.5	0.79	16.2	−16.1	0.76
4-Alkyl	3.1	−22.3	0.98	2.6	−21.0	0.95
3,3'-Dialkyl	16.0	−23.7	0.87	25.4	−14.2	0.60
3,4'-Dialkyl	12.3	−24.0	0.86	21.4	−21.0	0.73
4,4'-Dialkyl	2.6	−27.9	0.96	4.2	−29.6	0.94

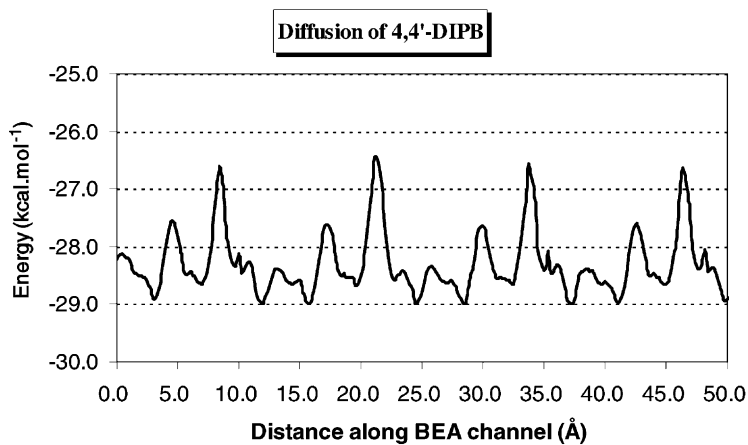


Fig. 3. Energy profile for the diffusion of 4,4'-DIPB in BEA zeolite.

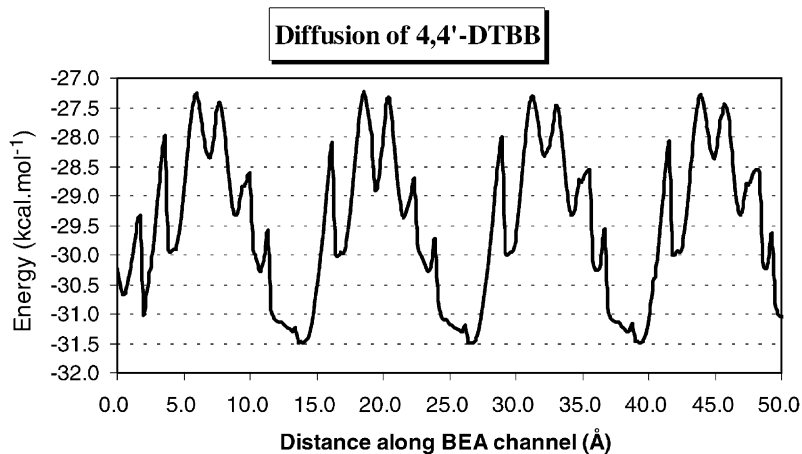


Fig. 4. Energy profile for the diffusion of 4,4'-DTBB in BEA zeolite.

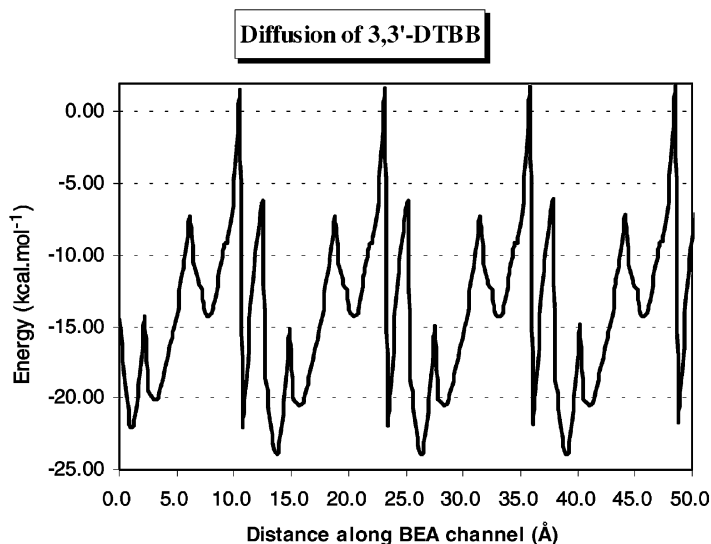


Fig. 5. Energy profile for the diffusion of 3,3'-DTBB in BEA zeolite.

Although there is more empty space available in BEA than in MOR, the energy barrier values calculated for *tert*-butylbiphenyls are very close to those obtained for MOR zeolite (Table 1). Thus, diffusivity for possible isomers in channel of BEA zeolite stands in the same order 4-MTBB > 4, 4'-DTBB > 3-MTBB > 3, 4'-DTBB > 3, 3'-DTBB.

The energy barriers calculated from energy diffusional profiles drawn for isopropylbiphenyl isomers stay in the same order as those calculated for *tert*-butylbiphenyl isomers (Table 2). It was found that 4-MIPB has the lowest energy barrier (3.1 kcal/mol) among MIPBs and 4,4'-DIPB (2.6 kcal/mol) among DIPBs. Thus, the flexibility of studied isopropylbiphenyl isomers is in the order *para* > *meta* > *ortho*.

These results observed on the basis of molecular modelling predict that BEA zeolite could be a potential catalyst for shape-selective isopropylation as well as for *tert*-butylation of biphenyl with a preferential formation of 4- and 4,4'-isomers, although pore architecture and pore sizes of BEA zeolite are quite different from those of MOR.

3.3. Comparison of computational and experimental results

To compare the experimental results with the computational, two zeolites of different structures

(H-MOR (17.5) and H-BEA (12.5)), but with comparable silica/alumina molar ratio were chosen. Reactions of isopropylation and *tert*-butylation of biphenyl have been carried out under the same reaction conditions [16–18].

Both, H-MOR (17.5) and H-BEA (12.5) zeolites are shown to be more active for *tert*-butylation of biphenyl. A maximum of 67% for the biphenyl conversion is obtained in *tert*-butylation after 8 h reaction over H-MOR (17.5), whereas in the isopropylation reaction, such a maximum for the biphenyl conversion is 41%. The same result is observed for H-BEA (12.5) (54% of biphenyl conversion in *tert*-butylation after 8 h reaction versus 35% in isopropylation). Such a result is explained by the higher reactivity of the *tert*-butyl carbocation in comparison with the isopropyl one.

The distribution of MTBB and DTBB derivatives over H-MOR (17.5) and H-BEA (12.5) zeolites together with the corresponding energy barriers and kinetic diameters are listed in Table 3.

The prediction made by using molecular modelling is in good agreement with the experimental results achieved in the *tert*-butylation of biphenyl over H-MOR (17.5) as well as over H-BEA (12.5) (Table 3).

H-MOR (17.5) has been found to be very shape-selective for the studied reaction. Among

Table 3

Distribution of the products in the *tert*-butylation of biphenyl over H-MOR (17.5) and H-BEA (12.5) and their calculated kinetic diameters and energy barriers

Molecule	Kinetic diameter (Å)	H-MOR		H-BEA	
		Barrier (kcal/mol)	Distribution ^a (%)	Barrier (kcal/mol)	Distribution ^a (%)
4- <i>tert</i> -Butyl	5.8	3.8	52.3	2.6	56.5
4,4'-Di- <i>tert</i> -butyl	5.8	1.1	46.9	4.2	17.8
3- <i>tert</i> -Butyl	7.5	4.3	0.8	16.2	20.2
3,4'-Di- <i>tert</i> -butyl	7.8	17.2	0	21.4	5.4
3,3'-Di- <i>tert</i> -butyl	7.9	31.2	0	25.4	0

^a Reaction conditions: catalyst, 0.5 g; BP, 10 mmol; *tert*-butanol, 20 mmol; *T*, 160 °C; *p*, 3.5 MPa; *n*-decane, 100 ml; conversion of biphenyl (X_{BP}), 35%.

MTBBs, 4-MTBB is formed preferentially (52.3% of 4-MTBB against 0.8% of 3-MTBB at a biphenyl conversion of 35%) and in the case of DTBB isomers, only 4,4'-DTBB is obtained. Thus, it is confirmed that 4-MTBB having the smallest kinetic diameter (5.8 Å) and the lowest energy barrier (3.8 kcal/mol) can diffuse through pores of mordenite more easier than 3-MTBB with higher values of the kinetic diameter (7.5 Å) and the energy barrier (4.3 kcal/mol). The same result is achieved for di-*tert*-butylated derivatives, where the differences between the kinetic diameters of 4,4'-DTBB and the other DTBB isomers as well as between their energy barriers are significantly higher than for the MTBB isomers (Table 3). Such a result explains the selective formation of 4,4'-DTBB over H-MOR (17.5).

The experimental results obtained over H-BEA (12.5) for the *tert*-butylation of biphenyl (Table 3) also support the computational analysis. The main step is monoalkylation with the formation of 56.5% of 4-MTBB at a biphenyl conversion of 35%. Nevertheless, 3-MTBB is obtained also in a certain extent (20.2%) despite of higher values of its kinetic diameter (7.5 Å) and energy barrier (16.2 kcal/mol). Thus, pore dimensions of BEA zeolite ($5.7 \times 7.5 \text{ \AA}^2$) allow diffusion not only of 4-MTBB having the smallest kinetic diameter and energy barrier but 3-MTBB may also diffuse through the pores although it is more hindered. As for the dialkylation step, besides the formation of 4,4'-DTBB (17.8%), the formation of 3,4'-DTBB is also observed (5.4%). Although kinetic diameter of 3,4'-DTBB (7.8 Å) is larger than pore dimensions of BEA zeolite and its energy barrier is

high (21.4 kcal/mol), it can diffuse through the pores of BEA zeolite due to a possible conformational flexibility of this molecule, arising from the rotation of the two benzyl rings around the C₁–C_{1'} bond.

Concerning the isopropylation reaction, Table 4 shows the distribution of the MIPB and DIPB derivatives over H-MOR (17.5) and H-BEA (12.5) zeolites together with the corresponding energy barriers and kinetic diameters.

The distribution of the MIPB and DIPB isomers achieved over H-MOR (17.5) is in good agreement with the calculated values of the computational analysis. As shown in Table 4, 4-MIPB and 4,4'-DIPB having the smallest kinetic diameters and energy barriers are formed preferentially (34.3 and 41.8%, respectively). Nevertheless, 3-MIPB (12.4%) and 3,4'-DIPB (9.3%) are also formed, which was not observed in the *tert*-butylation reaction (Table 3). The differences between kinetic diameters of desired 4-MIPB and 4,4'-DIPB and their other isomers are not so significant as the differences between *tert*-butylbiphenyl isomers (for example, the difference in kinetic diameters of 4,4'-DTBB and 3,4'-DTBB is 2.0 Å, while such a difference between 4,4'-DIPB and 3,4'-DIPB is 1.2 Å). Moreover, except for the 4,4'-derivatives, the energy barriers of isopropylbiphenyl derivatives are lower in comparison with the energy barriers calculated for the *tert*-butylbiphenyls in MOR channel. Taking into account the pore dimensions of mordenite ($7.0 \times 6.5 \text{ \AA}^2$) and conformational flexibility of the molecules, 3-MIPB and 3,4'-DIPB can diffuse through its pores in spite they are more hindered than 4-MIPB and 4,4'-DIPB, respectively. On the other hand, the

Table 4

Distribution of the products in the isopropylation of biphenyl over H-MOR (17.5) and H-BEA (12.5) and their calculated kinetic diameters and energy barriers

Molecule	Kinetic diameter (Å)	H-MOR		H-BEA	
		Barrier (kcal/mol)	Distribution ^a (%)	Barrier (kcal/mol)	Distribution ^a (%)
4-4'-Diisopropyl	6.0	1.7	41.8	2.6	7.4
4-Isopropyl	5.9	2.2	34.3	3.1	33.8
3-Isopropyl	7.2	3.6	12.4	4.3	38.0
3,4'-Diisopropyl	7.2	6.8	9.3	12.3	12.2
3,3'-Diisopropyl	7.8	7.1	1.5	16.0	5.0
2-Isopropyl	8.4	12.3	0.7	36.1	3.5

^a Reaction conditions: catalyst, 0.5 g; BP, 10 mmol; *tert*-butanol, 20 mmol; *T*, 160 °C; *p*, 3.5 MPa; *n*-decane, 100 ml; conversion of biphenyl (X_{BP}), 35%.

formation of few amounts of 2-MIPB (0.7%) and 3,3'-DIPB (1.5%) achieved over H-MOR (17.5) could be explained by the involvement of the outer surface.

Although the computational results (Table 4) predict shape-selective behaviour of H-BEA zeolite for the isopropylation of biphenyl, the experimental results are somewhat different. The 3-MIPB and 3,4'-DIPB are formed in higher extent than the desired 4-MIPB and 4,4'-DIPB (38% of 3-MIPB against 33.8% of 4-MIPB, 12.2% of 3,4'-DIPB against 7.4% of 4,4'-DIPB, respectively). It is obvious that despite of higher energy barriers of 3-MIPB and 3,4'-DIPB in comparison with the energy barriers of 4-MIPB and 4,4'-DIPB (4.3 kcal/mol for 3-MIPB to 3.1 kcal/mol for 4-MIPB and 12.3 kcal/mol for 3,4'-DIPB to 2.6 kcal/mol for 4,4'-DIPB), these molecules can diffuse relatively easily through the pores of BEA zeolite. As it was mentioned above, the architecture of BEA zeolite consists of 12-membered ring openings with interconnected linear channels of $7.7 \times 6.6 \text{ \AA}^2$ and perpendicular connecting openings of $5.6 \times 5.6 \text{ \AA}^2$ [29]. Thus, in the BEA zeolite channels, there is enough space for the formation of 3-MIPB and 3,4'-DIPB isomers having a kinetic diameter of 7.2 Å; even the 3,3'-DIPB, which is obtained in a few amount (5%), is able to diffuse through the pores of H-BEA zeolite due to its conformational flexibility, although it is significantly hindered (the kinetic diameter of 3,3'-DIPB is 7.8 Å and its energy barrier is 16 kcal/mol). As in the case of H-MOR, the formation of the most sterically hindered isomer 2-MIPB (3.5%) over H-BEA (12.5) could be explained by involvement of the outer surface.

4. Conclusion

Force field minimization techniques have been shown to be useful tools for the study of diffusional behaviour of molecules in pores of zeolites. According to diffusional characteristics, such as energy barrier and diffusivity calculated for possible isopropylbiphenyl and *tert*-butylbiphenyl derivatives in MOR and BEA zeolite channels, these zeolites were predicted to be shape-selective catalysts for isopropylation and *tert*-butylation of biphenyl.

The smallest energy barriers and the highest diffusivities are obtained for 4- and 4,4'-isomers in MOR channel as well as in BEA.

The calculated results are in good agreement with the experimental results achieved in the *tert*-butylation of biphenyl over H-MOR (17.5) and H-BEA (12.5) zeolites. The 4-MTBB and 4,4'-DTBB having a kinetic diameter of 5.8 Å and the smallest energy barriers are formed preferentially over both zeolites. Nevertheless, 3-MTBB and 3,4'-DTBB are obtained in a certain extent over H-BEA (12.5); such a result is explained by the pore dimensions of this zeolite, which can accommodate these molecules despite their higher kinetic diameters and energy barriers.

In the case of isopropylation reaction, the experimental results achieved over H-MOR (17.5) are in a good agreement with the computational analysis, but besides the main products 4-MIPB and 4,4'-DIPB, 3-MIPB and 3,4'-DIPB are also formed, which was not observed in the *tert*-butylation reaction. The formation of the latter can be explained by the differences between kinetic diameters of desired

4-MIPB and 4,4'-DIPB and their other isomers which are not so significant as the differences between *tert*-butylbiphenyl isomers, together with energy barriers that are lower in comparison with the energy barriers calculated for the *tert*-butylbiphenyls in MOR channel. The experimental results observed over H-BEA (12.5) are somewhat different from the computational ones. The preferential formation of the more hindered 3-MIPB and 3,4'-DIPB despite their high energy barriers is explained by the special architecture of BEA zeolite which allows relatively easy diffusion of these molecules through the pores.

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