Molecular Modeling of Carbonaceous Compounds Formed Inside the Pores of FER Zeolite during Skeletal Isomerization of *n*-Butene

Patricia Andy, Dominique Martin, and Michel Guisnet

UMR 6503. Catalyse en Chimie Organique, Université de Poitiers, Faculté des Sciences,
40 avenue du Recteur Pineau, 86022 Poitiers Cedex, France

Robert G. Bell* and C. Richard A. Catlow

Davy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street,
*London WIX 4BS, UK*

Molecular mechanics calculations of isobutene, its dimer (2,4,4-trimethyl-2-pentene), its trimer (2,4,4,6,6-pentamethyl-2-heptene), and seven families of coke molecules formed during *n*-butene isomerization were carried out within the ferrierite pore system. Monte Carlo docking showed that most of these molecules are well solvated by the zeolite framework and are preferentially sited within one or two intersections along the 10-membered ring channel. The locations of most of the larger coke molecules in two adjacent intersections account for the significant influence of dehydrogenative coupling in the formation of coke molecules in FER-structured zeolites. The stability of the butene dimer is close to that of molecules of carbonaceous compounds, which are known to be trapped inside the zeolite pores, whereas the stability of a trimer intermediate is much lower. This is consistent with the bimolecular isomerization mechanism and autocatalytic process proposed previously. Of the coke molecules investigated, only fluoranthene is unstable in the FER pores. This suggests that fluoranthene is not completely located in the zeolite pores, and it is proposed that this molecule is formed at the pore mouth. The results of simulated diffusion calculations confirmed the minimum energy locations of biphenyl and naphthalene found by docking and were consistent with experimental data regarding the mobility of these two species in ferrierite.

I. Introduction

Throughout the 1990s, there has been an increasing demand for isobutene, which is used in the production of methyl tertiary butyl ether (MTBE), a gasoline additive with a high octane number and antipollutant properties.[1−3] As a result, new methods of producing isobutene, in particular involving the skeletal isomerization of *n*-butene, have been developed. A large variety of catalysts based on alumina[4−9] or on medium pore size zeolites and zeotypes[4,10−16] have been reported as being efficient for this isomerization. Among these zeolites, ferrierite, which contains intersecting 8-membered ring (3.4 × 4.7 Å) and 10-membered ring (4.2 × 5.4 Å) channels,[17] has been claimed to be highly active and selective to isobutene[13] under typical reaction conditions of 623 K and 1 bar. Consequently, a substantial amount of research has been carried out in order to understand the origin of this selectivity and thereby determine the isomerization mechanism and the active sites.

It has previously been shown that fresh H−FER catalyst is not selective to isobutene, but that the selectivity increases significantly with time-on-stream.[18] On the fresh catalyst, propene and pentenes appear as primary products, in addition to isobutene. *n*-Butane and a small amount of octenes are also directly formed. A dimerization−isomerization-cracking mechanism, in which the desorption of octenes is limited by the narrow size of the pores of H−FER, has been proposed to explain the simultaneous direct formation of isobutene, propene, pentenes, and small amounts of octenes.[19]

$$2n\mathrm{C_4^=} \rightleftharpoons \mathrm{C_8^=} \rightleftharpoons \mathrm{C_8'^=}$$
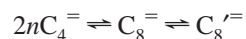
n-Butane is formed by hydrogen transfer from coke precursors to *n*-butene, as suggested by the deposit of carbonaceous compounds (coke) within the zeolite pores.[20]

The carbonaceous compounds (coke) were recovered from the zeolite pores after the dissolution of the coked zeolite in hydrofluoric acid solution and analyzed by GC/MS. Figure 1 shows the main families of carbonaceous compounds that were observed, as well as the scheme of coke formation that was proposed from the effect of time-on-stream on coke composition (Figure 2). Coke is constituted of slightly condensed aromatics (containing two to four aromatic rings) with methyl substituents (from 0 to 5). These coke molecules are formed by the transformation of benzenic products in two different ways: (i) the classical route *via* alkylation, cyclization, and hydrogen transfer steps; and (ii) the dehydrogenative coupling.[21] Curiously, dehydrogenative coupling, which generally plays a limited role in the formation of coke in other zeolites,[22] is implicated here in the formation of most of the coke molecules, as evidenced by the predominance of bridged aromatic species (families C to G in Figure 1). By contrast, in the zeolite H−TON under the same reaction conditions, the more fully condensed linear aromatics (e.g., naphthalene, anthracene, naphthacene, and their methyl derivatives) formed by the classical cyclization

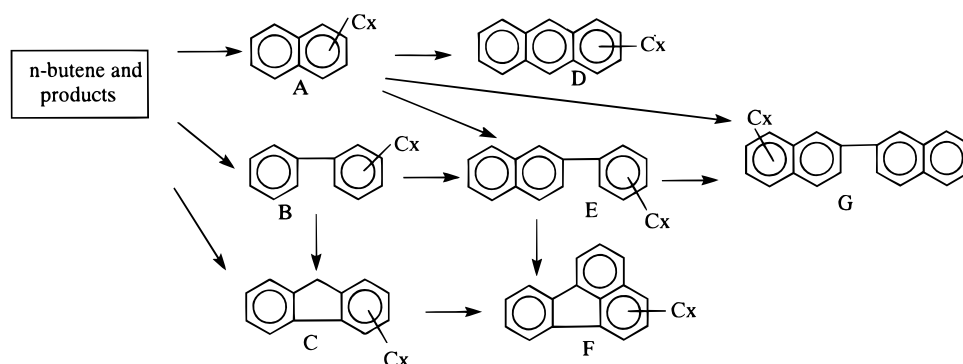* To whom correspondence should be addressed. Fax: +44 20 7629 3569. E-mail: rob@ri.ac.uk.

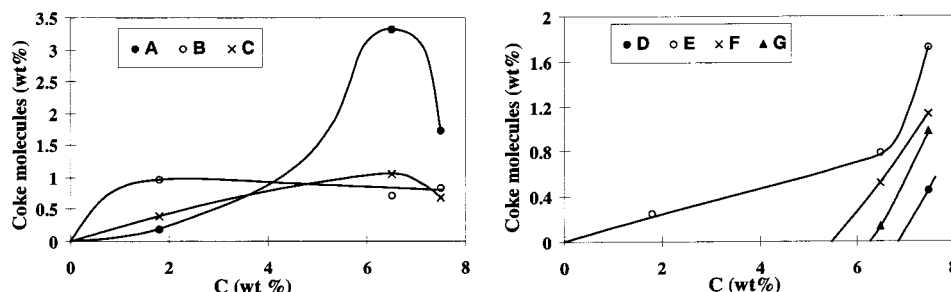**Figure 1.** Scheme of coke formation in FER.

Figure 2. Percentage of coke molecules of the seven families versus coke content.

mechanism make up the bulk of the coke molecules observed, with the anthracene family in particular predominating at long time-on-stream.[22] The TON framework structure contains only monodirectional 10-membered ring channels with no side pockets, or cross-linking by smaller pores.

The bimolecular isomerization process was shown to occur inside the zeolite pores. Indeed, the number of acid sites located on the outer surface of the crystallite is very limited, as is shown by the very low activity of the FER sample for isooctane cracking at 773 K.[15] Moreover, there is initially a significant decrease in the formation of isobutene, propene, and pentenes as time-on-stream, and hence, the coke content, increases. Nitrogen adsorption shows that this decrease is related to a blockage by coke of the access to the zeolite pores.[20] However, although the formation of propene and pentenes (and also *n*-butane) decreases continuously after a certain time-on-stream, dependent on the contact time, an increase in the formation of isobutene is observed. This increase, which is followed by a decrease at long time-on-stream, was explained by proposing a new mechanism in which the isomerization is catalyzed by carbonaceous compounds and/or reaction products retained inside the zeolite pores. It was proposed that, at short time-on-stream, the increase in isobutene yield was due to an autocatalytic reaction: *n*-butene isomerization occurring on *tert*-butylcarbenium ions formed by adsorption of isobutene molecules (which are slowly desorbed from the pores) on the protonic sites of the zeolite.[23] At long time-on-stream, the active species could be benzylic carbocations formed from carbonaceous compounds trapped in the pores near the outer surface of the crystallites.[21]

In this work, we have used molecular mechanics techniques[24,25] to determine preferred locations and binding energies of carbonaceous compounds within the pores of ferrierite and to probe the diffusion pathways of certain members of the aromatic species along the main 10-membered channel system. The main aims of the study are to investigate whether there are steric factors particular to the FER framework, which may explain the importance of dehydrogenative coupling in coke molecule formation and also, using the calculated data, to discuss
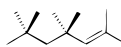
the effect of carbonaceous compounds and also of isobutene and of octenes on the rate of *n*-butene isomerization.

II. Methodology

Both the Monte Carlo docking and the forced diffusion (constrained minimization) procedures were used as implemented in software available from Molecular Simulations Inc.[26] All of the results were computed using the *cff9l_czeo* force field developed by Hill and Sauer,[27] in which bonded interactions are represented by 2, 3, and 4 body terms and nonbonded interactions by both 6−9 Lennard−Jones potentials and a Coulombic term. The zeolite host was assumed to be purely siliceous in composition.

1. Monte Carlo Docking. The minimum energy locations and binding energies of isobutene, 2,4,4-trimethyl-2-pentene, 2,4,4,6,6-pentamethyl-2-heptene, and coke molecules were investigated using a methodology that combines molecular dynamics, Monte Carlo simulation, and energy minimization. This method was employed first by Freeman et al.[28] and then by different authors[29−32] for docking molecules such as the four isomers of butene or templates used in zeolite synthesis. The procedure begins with a high-temperature molecular dynamics run for the sorbate molecule in vacuo, of which the resultant trajectory is sampled to produce a conformational library of the given molecule. In this work, the molecular dynamics simulations were carried out at 623 K using a 1 fs time step, with 100 conformations obtained by sampling every 100 fs for each molecule. The docking procedure itself then involves the random selection of positions and orientations for the sorbate molecule within the zeolite structure, which are screened by calculating only the van der Waals energy (i.e., the Lennard−Jones terms). For each conformation, the process continues until a satisfactory docked structure is achieved, with the van der Waals energy threshold being chosen for each molecule to give a sterically reasonable set of structures. Finally, each candidate's docked structure is subjected to optimization by energy minimization using the full force field, including the electrostatic term. In

TABLE 1: Minimum Energy of the Alkenes Inside the FER Zeolite[a]

	Isobutene (10MR/8MR)	Isobutene (6MR/8MR)	2,4,4-trimethyl-2-pentene	2,4,4,6,6-pentamethyl-2-heptene
Binding E (kJ mol⁻¹)	-45.1	-45.0	-41.2	-12.4

[a] (10MR/8MR) refers to location in the intersection between the 10-membered ring and eight-membered ring channels, (6MR/8MR) to the smaller cavities bounded by 6-rings and the eight-membered ring channel.

both the initial docking and the minimization stages, periodic boundary conditions were applied, using a supercell of the FER structure, doubled in the *c* direction (approximately 19.16 × 14.13 × 14.98 Å) and with no internal symmetry assumed. A cutoff of 7.0 Å (half the smallest cell parameter) was used for the van der Waals' terms. During minimization, the zeolite framework was allowed to relax in response to the presence of the guest molecule, and the coulomb term was evaluated using an Ewald summation.

The binding energy of the molecule inside the zeolite pore was taken as the minimized potential energy of the host−guest ensemble minus the potential energy of each component minimized separately using the same force field and simulation parameters.

$$E_b = E_{min}(host-guest) - E_{min}(host) - E_{min}(guest)$$

2. Diffusion (Constrained Minimization). These calculations were performed according to the forced diffusion procedure used by Horsley et al.[33] in a study of the shape-selective properties of zeolites in the alkylation of naphthalene. Here, the zeolite is represented as a discrete cluster rather than a periodic system. The dimensions of the clusters were chosen so as to permit the sorbate molecule to diffuse along a trajectory that is 20 Å in length, with a sufficient representation of the surrounding zeolite structure to satisfy a 9.5 Å van der Waals potential cutoff.

The diffusion path was defined by a pair of points lying at the center of the 10-membered ring channel and separated by 20 Å in the crystallographic ⟨001⟩ direction. At each step of the calculation, the molecule was constrained to lie at a fixed distance in *z* from these points by the application of a strong harmonic potential. The molecule was moved along the channel in increments of 0.2 Å, with the position of the sorbate being optimized with respect to the framework at each step. In these calculations, the framework was assumed to be rigid, and only the internal energy of the sorbate and the sorbate-framework van der Waals interactions were considered in the minimizations. The electrostatic term was neglected.

III. Results and Discussion

The minimum binding energy in ferrierite of various molecules that may be formed inside the zeolite pores was calculated using the Monte Carlo docking procedure. In the first stage, the molecules chosen were isobutene, its dimer (2,4,4-trimethyl-2-pentene), and its trimer (2,4,4,6,6-pentamethyl-2-heptene). Next, the main coke molecules (without methyl groups, for simplicity) were studied, including calculations of the diffusion profile for naphthalene and biphenyl. Finally, the effect of methyl substituents was included, again only for the simplest families of molecules, naphthalene and biphenyl.

For each molecule, the minimum binding energy given is the lowest out of 100 minimized structures. In the great majority of cases, several identical, or nearly identical, minimum-energy

structures were found, with the energies of the five lowest energy structures typically spanning a range of less than 2.5 kJ mol⁻¹. The major exception was isobutene itself, which exhibited several minima of very similar energy, in both the 10-ring and 8-ring pore systems.

1. Binding Energies of Isobutene, its Dimer, and its Trimer. The binding energies of isobutene, 2,4,4-trimethyl-2-pentene and 2,4,4,6,6-pentamethyl-2-heptene are given in Table 1. In the case of isobutene, two minimum energy positions are found: (i) at the intersection of the 8- and 10-ring channels and (ii) in the smaller cavities located along the 8-ring channels. The energy values and locations of isobutene are similar to those found by Jousse et al. (−44.6 kJ mol⁻¹ in the larger intersections and −49.3 kJ mol⁻¹ in the smaller intersections).[32] However, both the adsorption measurements of Xu et al.[34] and the molecular dynamics results of Jousse et al.[32] indicate that isobutene cannot access the smaller cavity sites. For 2,4,4-trimethyl-2-pentene, the minimum energy site lies along the 10-ring channel, straddling two adjacent intersections of 8- and 10-ring channels (Figure 3). Using the simulated diffusion procedure, Millini and Rossini[29] found the same position and almost the same minimum energy (−39.2 kJ mol⁻¹) for this dimer. The trimer is also optimally located in two adjacent intersections along the 10-ring channels. We note that although the minimum energy values are similar for isobutene and the dimer, the value found for the trimer is significantly lower in magnitude. Taking into account the number of carbon atoms in each molecule, it is apparent that the trimer is markedly less-well stabilized by the FER structure compared to the dimer, which is itself about half as well stabilized as two isobutene molecules.

2. Binding Energies and Diffusion Profiles of Coke Molecules (without Methyl Groups). The minimum energy values for the main families of coke molecules without methyl groups are presented in Table 2. Except for fluoranthene (family F) and 1-phenylnaphthalene (family E₂), the minimized binding energies for each molecule are of fairly high magnitude, suggesting that these molecules are reasonably well solvated by the FER framework. However, as there is no obvious correlation between molecular size and binding energy, we conclude that the smaller molecules, naphthalene (family A) and biphenyl (family B), are relatively better stabilized.
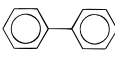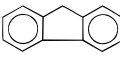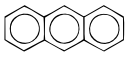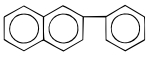
The minimum energy sites for naphthalene (family A) and fluorene (C) are centered within a single 8- to 10-ring channel intersection. For the other molecules, the preferred sites span two intersections along the 10-ring channel. Figure 4 shows, for example, the preferred location of naphthalene (family A), biphenyl (family B), and binaphthalene (family G) inside the pore system of ferrierite.

The diffusion of naphthalene and biphenyl was also investigated. The results confirm the preferred location of naphthalene in one intersection and of biphenyl in two intersections along the 10-ring channel. During the diffusion, naphthalene and
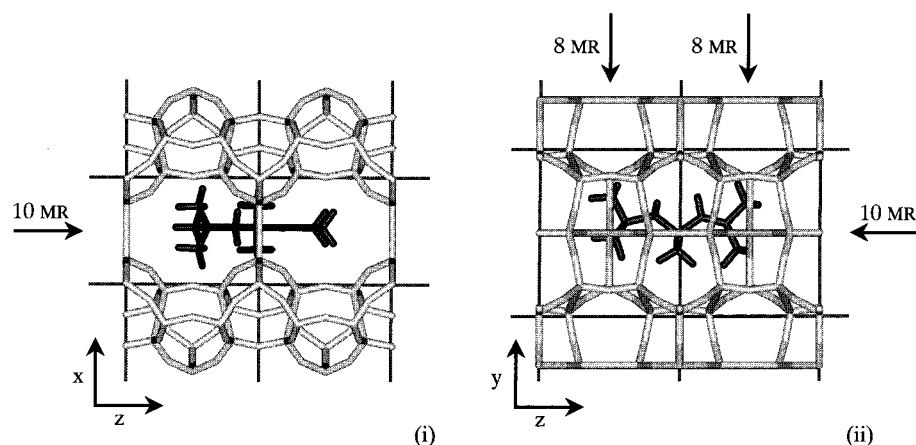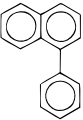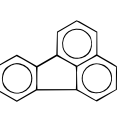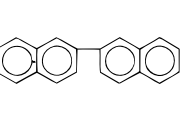
Figure 3. Minimum energy position of 2,4,4,6,6-pentamethyl-2-heptene inside the FER pore system. (i) View along [010]; (ii) view along [100].

TABLE 2: Minimum Energy of the Non-methylated Coke Molecules Inside the FER Pores

Family	A	B	C	D	E_1
x=0					
Binding E (kJ mol^{-1})	-78.1	-80.3	-54.8	-80.6	-66.5

Family	E_2	F	G
x=0			
Binding E (kJ mol^{-1})	-23.7	-8.7	-84.3

biphenyl molecules encounter energy barriers of 120 and 35 kJ mol^{-1}, respectively (Figures 5 and 6). The high value found for naphthalene suggests that its diffusion in the ferrierite pores is likely to be very limited, and moreover from the simulated trajectory it can be seen that the maximum point of the energy profile corresponds to the position of the channel intersection. On the other hand, the low-energy barrier found for biphenyl indicates that this compound can diffuse more easily in the pores because it encounters a much flatter potential energy surface. This could readily explain the observation that only a small amount of this compound (compared to mono- or bimethyl-substituted derivatives) remains blocked in the zeolite pores and is consistent with the proposal of a "supermobility" of this molecule.[33,35,36]
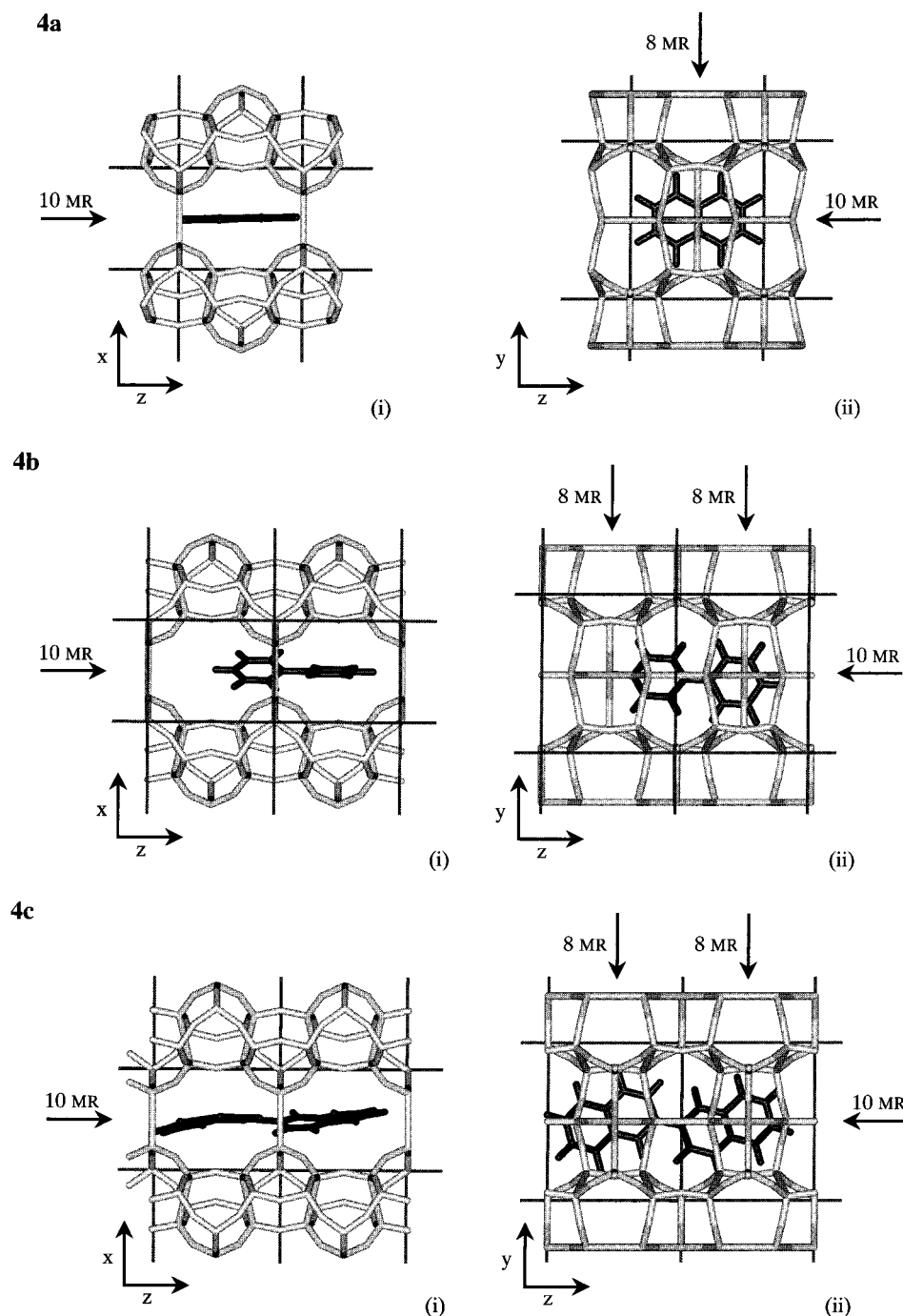
3. Binding Energies of Coke Molecules, including the Effects of Methyl Groups. The minimum energies of molecules with the same aromatic skeleton, but with differing numbers of methyl substituents (x), can be compared as follows: (1) As x increases, the minimized binding energy of the molecule should be of greater magnitude for an equivalent level of solvation. This takes into account that, for these sorts of molecule, the van der Waals energy is the dominant component of the binding energy. (2) For molecules that have the same number of carbons (i.e., the same value of x), the more stable molecule inside the zeolite corresponds to that which has the more negative minimum energy.

The binding energies for various methyl-substituted naphthalene molecules are given in Table 3. 2-methylnaphthalene (2-MN) is more stable than 1-methylnaphthalene (1-MN), which

could account for the much larger percentage of 2-MN in coke compared to 1-MN. In the other calculations, we have therefore only considered the docking of polymethylated molecules having one methyl in position 2. In the dimethylnaphthalenes, which are the main components of family A of coke (60% at 6.5 wt % coke), 2,6-dimethylnaphthalene (2,6-DMN) is the more stable. When the number of carbon atoms is considered, it can be inferred that its stability is very close to that of 2-MN. It is, thus, credible that 2,6-DMN is the dominant DMN component observed (but not identified) by mass spectrometry. 2,4,6-trimethylnaphthalene also seems very stable in FER, whereas 2,3,6-TMN is much less stable. Above three methyl groups, the minimum energy becomes less negative, due to increasing steric constraints, becoming slightly endothermic for 1,3,5,6,7-pentamethylnaphthalene. This low stability of tetra- and pentamethylnaphthalene is consistent with their presence in coke at only trace levels. For all of the methylnaphthalene molecules, the minimum energy site lies inside one intersection along the 10-ring channel.

In family B (biphenyl), the stability of the methylated compounds increases up to $x = 2$ (Table 4). This is consistent with methyl- and dimethylbiphenyl being the most favored members of family B. Among the monomethylated compounds, again it is the compound most linear in shape, 3-methylbiphenyl, that exhibits the highest stability; the other two isomers encounter a greater degree of constraint within the 10-ring channel. Broadly speaking, the minimum energy sites for all molecules in family B are located in the 10-ring channel between two intersections.

Molecular Modeling of Carbonaceous Compounds

J. Phys. Chem. B, Vol. 104, No. 20, 2000 **4831**

4a

4b

4c

Figure 4. Minimum energy positions of (**a**) naphthalene, (**b**) biphenyl, and (**c**) binaphthalene inside the FER pore system. (i) View along [010]; (ii) view along [100].

Minimum Binding Energy and Mechanisms of Butene Isomerization and Coke Formation. Direct comparison between the calculated binding energies of the various molecules is difficult because of their varying composition and the fact that carbon is present with different hybridizations. However, as an approximate guide to the relative level of solvation of each molecule by the FER framework, the binding energies per C atom have been calculated for the nonmethylated parent compound of each family and for isobutene and its dimer and trimer. These are shown in Figure 7.

On this basis, it can be proposed that isobutene, 2,4,4-trimethyl-2-pentene, naphthalene (A), biphenyl (B), anthracene (D), fluorene (C), phenylnaphthalene (E), and binaphthalene (G) are all likely to be present, at some level, within the FER pores

(assuming that other thermodynamic or kinetic factors do not disfavor their formation). In contrast, the much lower values for the isobutene trimer and for fluoranthene (F) suggest that those molecules cannot be located (at least completely) inside the zeolite pores. The possible formation of 2,4,4 trimethyl-2-pentene inside the pores is in agreement with the proposal of a bimolecular mechanism with autocatalysis.[23] The formation of trimer intermediates is strongly disfavored, although they are formed with other medium-pore sized zeolites: EU-1, MFI, and MTT.[15]

The presence of most of the coke molecules inside the zeolite pores has been previously confirmed by experiment, although it should be borne in mind that only a very small amount (<5%) can be recovered through a direct Soxhlet treatment of the coked
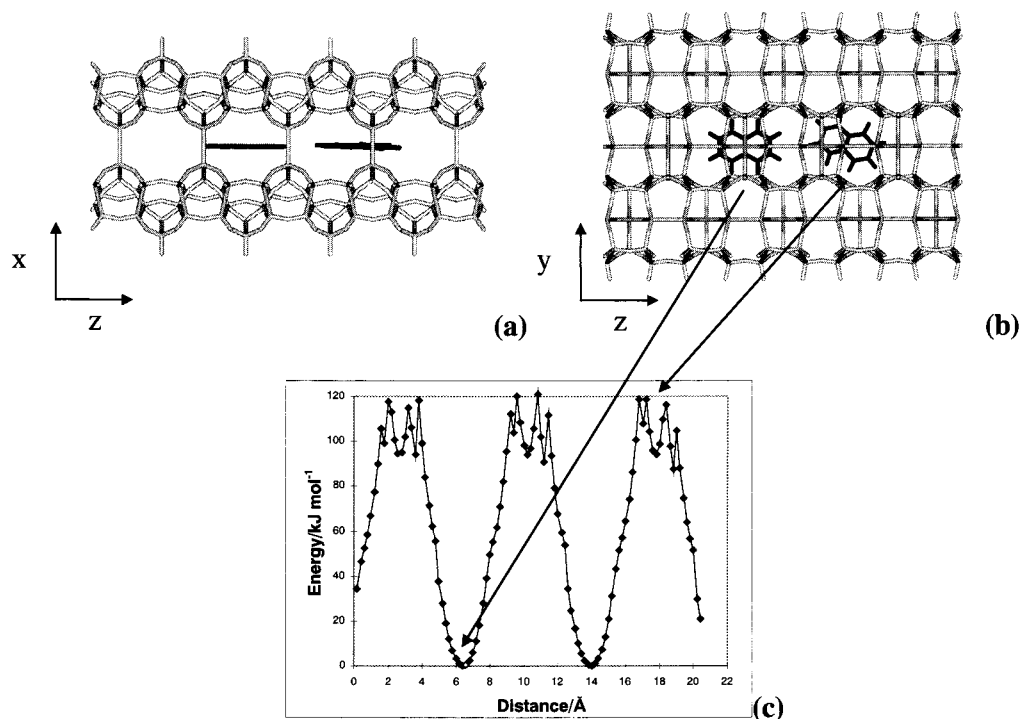
Figure 5. (**a** and **b**) Locations of naphthalene inside the pore system of FER and (**c**) relative energy of the molecule versus distance along the 10-membered ring channel. Minimum energy position: in one intersection. Maximum energy position: between two intersections.
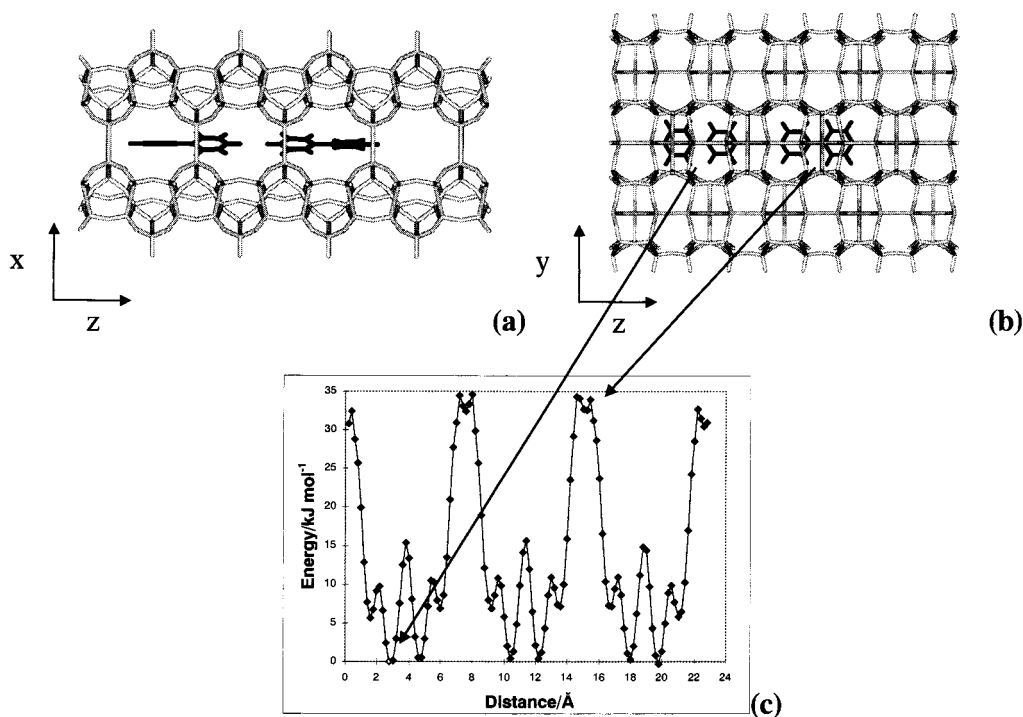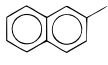

Figure 6. (**a** and **b**) Locations of biphenyl inside the pore of FER and (**c**) relative energy of the molecule versus distance along the 10-membered ring channel. Minimum energy position: between two intersections. Maximum energy position: in one intersection.

zeolite[21] (without previous dissolution of the zeolite in hydrofluoric solution). Furthermore, it should be noted that our arguments are based solely on the binding energies of the molecules within the zeolite framework. No account has been taken of the detailed mechanisms of coke formation in FER (as yet largely unknown). The precise thermodynamic profiles of these mechanisms would obviously also have a strong influence on the product distribution. Nevertheless, it should be emphasized that the main coke components observed
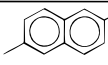
(families A and B) (Figure 2) are those for which we predict the most favorable binding energies (Figure 7 and Tables 3 and 4). Similarly, within these families, the principal compounds found are those for which the binding energy per carbon atom is more negative: dimethylnaphthalene (-8 kJ(mol·C)$^{-1}$ for 2,6-DMN) and methyl- and dimethylbiphenyl (-7.3 kJ(mol·C)$^{-1}$ for 3-methylbiphenyl and for 3,3-dimethylbiphenyl).
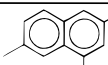
Among the coke molecules, those of family F exhibit a low stability due to steric constraints. In fact, this is reflected in the
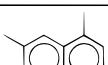
Molecular Modeling of Carbonaceous Compounds

J. Phys. Chem. B, Vol. 104, No. 20, 2000 **4833**

TABLE 3: Minimum Energy of the Molecules of Family A Inside the FER Pores

x=0	
Binding E (kJ mol^{-1})	-78.1

x=1		
Binding E (kJ mol^{-1})	-80.2	-66.5

x=2					
Binding E (kJ mol^{-1})	-96.3	-74.6	-71.2	-52.5	-51.6

x=3		
Binding E (kJ mol^{-1})	-90.0	-64.8

x=4			
Binding E (kJ mol^{-1})	-59.3	-58.5	-32.5
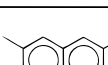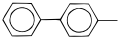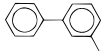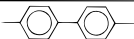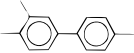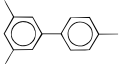
x=5		
Binding E (kJ mol^{-1})	-21.1	0.8

TABLE 4: Minimum Energy of the Molecules of Family B Inside the FER Pores

x=0	
Binding E (kJ mol^{-1})	-80.3

x=1			
Binding E (kJ mol^{-1})	-94.8	-74.3	-53.3

x=2	
Binding E (kJ mol^{-1})	-101.7

x=3		
Binding E (kJ mol^{-1})	-99.3	-82.8

Figure 7. Minimum energy per carbon of the non methylated aromatic compounds of families A, B, C, D, E, F, and G and of isobutene, its dimer, and its trimer.

simulations, which show a high, positive internal energy for the molecule, as it distorts somewhat from its ideal gas phase shape, to be accommodated within the pores. It therefore seems unlikely that these molecules (family F) are present to any significant degree within the bulk of the zeolite. However, these molecules could be formed from the transformation of fluorene or phenylnaphthalene molecules located near the pore mouth, with partial overflowing of the molecules outside of the pores. Indeed, molecules of family F appear only at long periods of time-on-stream and, hence, at high coke content when the pores are nearly completely filled with coke molecules.[21] This same

proposal, overflowing of the molecules outside the pores, could also explain why anthracene compounds (family D) appear only at very high coke contents by growth of naphthalene molecules near the pore mouth. This hypothesis seems less likely for the formation of binaphthalene molecules, as these molecules can result not only from the growth of phenylnaphthalene molecules located near the pore mouth but also from dehydrogenative coupling of two naphthalene molecules located in adjacent intersections. Indeed, this latter mechanism has the advantage that the binaphthalene molecules may be formed in situ in their most thermodynamically favored position. The overflow of coke molecules at the surface is in agreement with the strong increase in the C/Si ratio, found by XPS at high coke content.[37]

There are two routes for the growth of coke molecules. The first route is via successive alkylation, cyclization, and hydrogen transfer steps and the second involves dehydrogenative coupling of coke molecules. With most of the zeolite catalysts, the first route is favored, whereas with ferrierite dehydrogenative coupling is predominant. This coupling is implicated in the formation of all of the coke molecules formed during butene isomerization, with the exception of those of families A and D. The predominance of this mechanism in ferrierite was attributed to the proximity of adjacent channel intersections. The modeling results described here fully support this hypothesis, in that the molecules of families B, E, and G are preferentially located in two adjacent intersections (with the C−C bond linking the two aromatic rings between these two intersections), whereas the compounds from which they are formed, methyl-substituted benzenes and methylnaphthalene, have their minimum-energy sites at one intersection. The one slight anomaly concerns the molecules of family C, whose preferred site is centered at one intersection, whereas they result from transformation of biphenyl or diphenylmethane molecules whose minimum energy positions lie between two intersections. However, as described above, we predict a relatively flat potential energy surface for biphenyl within the 10-ring channel, suggesting that, at reaction temperatures, it may, in reality, populate a number of sites.

IV. Conclusion

From our modeling studies of various molecules within the FER pore system, the following main conclusions can be drawn: (1) The stability of 2,4,4-trimethyl-2-pentene is close to that of molecules of carbonaceous compounds (coke) that have been demonstrated to be formed and trapped inside the zeolite pores, whereas the stability of a trimer intermediate is much lower. This supports the bimolecular dimerization−isomerization-cracking mechanism with an autocatalytic process that has been previously proposed to explain the selective isomerization of *n*-butene into isobutene over aged ferrierite samples. (2) The minimum energy locations of coke molecules have been calculated. Although naphthalene and fluorene coke components are sited in one intersection of the 8- and 10-membered ring channels along the 10-membered ring channel, the other coke molecules are located in two adjacent intersections. Moreover, the very low stability of fluoranthene coke components suggests that these compounds are not completely located in the zeolite pores. It is suggested that these coke molecules are formed at the pore mouth and overflow outside the pore system. (3) The location of most of the coke molecules in two adjacent intersections accounts for the significant influence of dehydrogenative coupling in the formation of coke molecules in the ferrierite pores.

References and Notes

(1) Juguin, B.; Torck, B.; Martino, G. In *Catalysis by Acids and Bases*; Imelik, B., Naccache, C., Coudurier, G., Ben Taarit, Y., Vedrine, J. C., Eds.; (*Stud. Surf. Sci. Catal.*, Vol. 20); Elsevier: Amsterdam, 1985; p 253.

(2) Maxwell, I. E.; Naber, J. E.; de Jong, K. P. *Appl. Catal., A: General* **1994**, *113*, 153.

(3) Torck, B. *L'Actualité Chimique* **1997**, 3.

(4) Butler, A. C.; Nicolaides, C. P. *Catal. Today* **1993**, *18*, 443.

(5) Choudhary, V. R.; Doraiswamy, L. K. *J. Catal.* **1971**, *23*, 54.

(6) Juguin, B.; Miguel, J., European Patent No. 66485, 1982, Institut Français du Pétrole.

(7) Cheng, Z. X.; Ponec, V. *J. Catal.* **1994**, *148*, 607.

(8) Szabo, J.; Perrotey, J.; Szabo, G.; Duchet, J. C.; Cornet, D. *J. Mol. Catal.* **1991**, *67*, 76.

(9) Catani, R.; Cornaro, U.; Miglio, R.; Piccoli, V.; Rossini, S.; Finochio, E.; Busca, G. In *International Symposium on Acid−Base Catalysis III − Book of Abstracts*; Rolduc, Netherlands, 1997; p O26.

(10) Houzvicka, J.; Hansildaar, S.; Ponec, V. *J. Catal.* **1997**, *167*, 273.

(11) Mériaudeau, P.; Anh, T. Vu.; Hung, N. Le; Szabo, G. *Catal. Lett.* **1997**, *47*, 71.

(12) Asensi, M. A.; Corma, A.; Martinez, A. *J. Catal.* **1996**, *158*, 561.

(13) Mooiweer, H. H.; de Jong, K. P.; Kraushaar-Czarnetzki, B.; Storck, W. H. J.; Krutzen, S. C. H. In *Zeolites and Related Microporous Materials: State of the Art 1994*; Weitkamp, J., Karge, H. G., Pfeifer, H., Hölderich, H., Eds.; (*Stud. Surf. Sci. Catal.*, Vol 84); Elsevier: Amsterdam, 1994; p 2327.

(14) O'Young, C. L.; Pellet, R. J.; Casey, D. G.; Ugolini, J. R.; Sawicki, R. A. *J. Catal.,* **1995**, *151*, 467.

(15) Andy, P.; Gnep, N. S.; Benazzi, E.; Travers, C.; Guisnet, M. In *Proceedings of the DGMK Conference "C₄ Chemistry-Manufacture and Use of C₄ Hydrocarbons"*; Aachen, 1997; p 43.

(16) Woo, H. C.; Lee, K. H.; Lee, J. S. *Appl. Catal., A: General* **1996**, *134*, 147.

(17) Vaughan, P. A. *Acta Crystallogr.* **1966**, *21*, 983.

(18) Guisnet, M.; Andy, P.; Gnep, N. S.; Travers, C.; Benazzi, E. *J. Chem. Soc., Chem. Commun*, **1995**, 1685.

(19) Guisnet, M.; Andy, P.; Gnep, N. S.; Benazzi, E.; Travers, C. *J. Catal.* **1996**, *158*, 551.

(20) Guisnet, M.; Andy, P.; Gnep, N. S.; Travers, C.; Benazzi, E. In *Progress in Zeolite and Microporous Materials*; Chon, H., Ihm S.-K., Uh, Y. S., Eds.; (*Stud. Surf. Sci. Catal.*, Vol 105); Elsevier: Amsterdam, 1997; p 1365.

(21) Andy, P.; Gnep, N. S.; Guisnet, M.; Benazzi, E.; Travers, C. *J. Catal.* **1998**, *173*, 322.

(22) Andy, P. Ph.D. Thesis, University of Poitiers, 1998.

(23) Guisnet, M.; Andy, P.; Boucheffa, Y.; Gnep, N. S.; Travers, C.; Benazzi, E. *Catal. Lett.* **1998**, *50*, 159.

(24) Catlow, C. R. A., Ed. *Modelling of Structure and Reactivity in Zeolites*; Academic Press: London, 1992.

(25) Catlow, C. R. A. In *Handbook of Heterogeneous Catalysis*; Ertl, G., Knözinger, H., Weitkamp, J., Eds.; Vol. 3; Wiley−VCH: Weinheim, 1997; p 1149.

(26) (a) *Discover User Guide*, Version 3.0; MSI: San Diego, 1996. (b) *Catalysis User Guide*, Version 4.0.0; MSI: San Diego, 1996.

(27) (a) Hill, J.-R.; Sauer, J. *J. Phys. Chem.* **1994**, *98*, 1238. (b) Hill, J.-R.; Sauer, J. *J. Phys. Chem.* **1995**, *99*, 9535.

(28) Freeman, C. M.; Catlow, C. R. A.; Thomas, J. M. *Chem. Phys. Lett.* **1991**, *186*, 137.

(29) Millini, R.; Rossini, S. In *Progress in Zeolite and Microporous Materials*; Chon, H., Ihm S.-K., Uh, Y. S., Eds.; (*Stud. Surf. Sci. Catal.*, Vol 105); Elsevier: Amsterdam, 1997; p 1389.

(30) Bell, R. G.; Lewis, D. W.; Freeman, C. M.; Thomas, J. M.; Catlow, C. R. A. In *Zeolites and Related Microporous Materials: State of the Art 1994*; Weitkamp, J., Karge, H. G., Pfeifer, H., Hölderich, H., Eds.; (*Stud. Surf. Sci. Catal.*, Vol 84); Elsevier: Amsterdam, 1994; p 2075.

(31) Jousse, F.; Leherte, L.; Vercauteren, D. P. *Mol. Simul.* **1996**, *17*, 175.

(32) Jousse, F.; Leherte, L.; Vercauteren, D. P. *J. Mol. Catal. A: Chemical* **1997**, *119*, 165.

(33) Horsley, J. A.; Fellmann, J. D.; Derouane, E. G.; Freeman, C. M. *J. Catal.* **1994**, *147*, 231.

(34) Xu, W. Q.; Yin, Y. G.; Suib, S. L.; O'Young, C. L. *J. Phys. Chem.* **1995**, *99*, 9443.

(35) Derouane, E. G.; Andre, J.-M.; Lucas, A. A. *J. Catal.* **1988**, *110*, 58.

(36) Derouane, E. G. In *Guidelines for Mastering the Properties of Molecular Sieves*; Barthomeuf, D., Derouane, E. G., Hölderich, W., Eds.; (NATO ASI Series B.; Physics, Vol. 221); Plenum Press: New York, 1990; p 225.

(37) de Jong, K. P.; Mooiweer, H. H.; Buglass, J. G.; Maarsen, P. K. In *Catalyst Deactivation 1997*; Bartholomew, C. H., Fuentes, G. A., Eds.; (*Stud. Surf. Sci. Catal.*, Vol. 111); Elsevier: Amsterdam, 1997; p 127.