

A New Automated Molecular Modeling Method to Locate Coke and to Follow Its Growth Inside Zeolite: Application to the Coke Formed during the Transformation of Toluene on H-MFI

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A new automated molecular modeling method was developed to locate coke molecules and to follow their growth inside zeolites using the Cerius2 software from MSI. This method is based on the consecutive use of isothermal molecular dynamic (NVT), Monte Carlo simulation (sorption), and energy minimization procedures. The Cerius2 software scripting capacity combined with the Tool command language (Tcl) is used to automate the procedure. The results obtained on the location of coke molecules formed during toluene transformation at low and high temperatures demonstrate the interest of the method. Moreover, the sorption procedure used here is particularly useful to specify the mode of growth of coke molecules formed inside the zeolite pores. © 1999 Academic Press

Key Words: molecular modeling; coke location; coke growth; zeolites; H-MFI; toluene.

1. INTRODUCTION

Acid zeolite catalysts are used in numerous refining (e.g., cracking, hydrocracking) and petrochemical (e.g., isomerization and disproportionation of aromatics) processes. In the corresponding acid-catalysed reactions the formation of carbonaceous compounds (coke) is the main cause of zeolite deactivation. Most of these compounds are formed inside the pores, where they remain blocked due to their adsorption or volatility (low-temperature coke) or to steric blockage (high-temperature coke) (1). One of our research interests is to determine how the size and the shape of zeolite pores determine the composition of coke, the location of coke molecules, and their deactivating effect (2–7). The study was carried out over various zeolites with small (ERI), medium (MFI, FER, MWW), and large (FAU, MOR, OFF) pore apertures during propene, butene, *n*-heptane, and toluene transformation under a large range of operating conditions (at particular temperatures). The composition of coke was determined using a method developed in our laboratory (8), and the location of coke molecules was deduced from the comparison between their

size and shape and those of the zeolite channels and cages, and from sorption experiments with probe molecules of different sizes (6).

Molecular modeling is well adapted to specify the exact location of coke molecules inside the zeolite void space (channels and cages). The simplest method that can be used is to place the coke molecule in its lower conformation (relaxed) inside the zeolite channels or cages and to minimize in energy the host-guest system. However, two major problems occur with this method. The first one is that the relaxed conformation of the coke molecule is not always the more appropriate to fit in with the void space inside the zeolite structure. The second problem concerns the choice of the initial position of the coke molecule inside the zeolite channels. To solve these problems, we have recently developed an automated method adapted from the docking procedure first used by Freeman *et al.* (9). This method, described in detail in the next section, is based on the consecutive use of Molecular Dynamic (MD), Monte Carlo (MC), and Energy Minimization (EM) procedures. This new method is used to locate the coke molecules formed during toluene transformation over an H-MFI zeolite, which allowed us to visualize the formation of the first molecules inside the zeolite pores, as well as their growth. This representation of coking at the molecular scale should be particularly useful to the understanding of the influence of the pore structure and, inversely, in discriminating between proposed structures for new zeolites.

2. METHODOLOGY

2.1. General Considerations

As previously noted, the method is adapted from the docking procedure developed by Freeman *et al.* for determining the minimum energy position of butene isomers inside the MFI pore system (9). The docking procedure is now totally implemented in the Insight II software of Molecular

Simulation Inc. (MSI). It has been used by many teams for locating butene molecules in DAF-1 (10), medium pore size zeolites (11, 12), and potential template molecules for synthesizing zeolites (13–15). In all our molecular modeling experiments, the Cerius2 software, also developed by MSI, was used. In Cerius2, the automated docking procedure is not implemented. The Cerius2 scripting capacity allows us, using the Tool command language (Tcl), to write scripts used to run automated procedures in the background. From these scripts, calculations of the minimum energy locations of the coke molecules are carried out and, if it is necessary, the growth of coke molecules can be followed inside the zeolite pores.

The two problems, mentioned in the introduction, concerning the molecular modeling of the location of coke molecules are solved as follows. Concerning the conformation of coke molecules, the procedure starts with a high-temperature (1500 K) isothermal molecular dynamic (NVT) of the coke molecule alone. An isothermal dynamic is chosen because it can be more useful than an adiabatic molecular dynamic (NVE) as a way to sample conformational space (during NVT, the energy can be taken from a heat bath to overcome rotational barriers). This NVT generates a trajectory file by storing a number of the representative conformational possibilities of the coke molecules.

These conformational possibilities will be extracted and used as candidates for the sorption (Monte Carlo) procedure within the zeolite pores. While the generation of the conformational possibilities of the coke molecules is based on a method similar to that used by Freeman *et al.* (9), the sorption procedure (Monte Carlo) is different. With Cerius2, the fixed loading (canonical ensemble) simulation with one coke molecule can be used to find the more appropriate location for each conformation of coke molecules inside the zeolite void space. The initial configuration is generated as follows. The initial coordinates of the sorbate in the zeolite pore system are the same as the coordinates of the sorbate from the NVT trajectory. In this way, to begin the sorption we can place the coke molecule in a chosen position inside the zeolite pores. Either a random translation or a rotation of the sorbate molecule generates each subsequent configuration. Each generated configuration is accepted or rejected using a Metropolis (16) algorithm based on the configurational energy change. The sorption takes a number of steps (1500) to equilibrate from its initial position; this equilibration is achieved when the configurational energy is constant. Forty to fifty percent of the configurations generated by translation or rotation are generally accepted.

Finally each host-guest system generated during the sorption procedure is relaxed (EM). During this EM both the coke molecule and the zeolite are relaxed. The minimization proceeds using the conjugate gradient algorithm. It terminates either after 1000 steps or when the energy con-

verges, i.e., when the root mean square (RMS) force is below a specified value (0.02 kcal/mol/Å). Then, the energy of the system is collected and the interaction energy could be calculated. Here, the interaction energy (E_i) is the energy of the host-guest system (E_{hg}) minus the energy of the zeolite (E_z) and of the sorbate (E_s) evaluated separately ($E_i = E_{hg} - E_z - E_s$). A negative interaction energy (E_i) means that the van der Waals interactions stabilize the coke molecules inside the zeolite pores. The lower the negative energy, the better the stabilization, hence the more favoured the location of the coke molecule. The Tool command language (Tcl) is used here to write the script, allowing us to run in the background the successive procedures described above, NVT, MC, and EM.

2.2. Calculations

All the calculations are based on an energy expression determined using the Burchart 1.01–Dreiding 2.21 force field written for the study of interactions between organic molecules and silico-aluminophosphate compounds. This force field is a combination of the Burchart (17) and Dreiding II (18) force fields. The Burchart force field is related to the zeolite framework. The Dreiding II force field is related to the intra- and intermolecular interactions. The parameters for the framework–molecule interactions are derived from the parameters of both force fields, combined through the usual arithmetic combination rule. The energy expression built from this force field is the sum of valence terms (bond, angle, torsion, inversion, and Urey–Bradley) and of nonbonded terms. The nonbonded term consists only of the van der Waals interactions. For sake of simplicity and because the formation and the location of the coke molecules are mainly determined by steric constraints, the zeolite framework is taken as purely siliceous (Al atoms then protons are absent), hence the Coulomb term is not included in the nonbonded terms of the energy expression. This model is validated by the results obtained by Jousse *et al.* (12). Using the docking procedure and allowing the relaxation of the zeolite structure with the sorbed molecule, these authors show that the location of butene isomers are the same inside purely siliceous Ferrierite and inside an acidic Ferrierite. Concerning the van der Waals energy term, the spline switching method is applied (cutin = 5.00 Å and cutoff = 9.95 Å), and the periodic boundary condition is assumed using the minimum image convention. All the calculations were performed using the 1.6 release of Cerius2 on an IBM RS/6000 model 350 computer with 64 Mb of memory.

A purely siliceous superlattice ($1 \times 1 \times 2$) of MFI built from the crystallographic data included in the zeolites library of the software is considered. It corresponds to a $20.022 \times 19.899 \times 26.766$ Å box. This superlattice and all the coke molecules, built using the 3D-Sketcher, are first

relaxed until the RMS force is lower than 0.02 kcal/mol/Å. For each coke molecule, 1 ps molecular dynamic with a 1 fs time-step is performed at 1500 K in the NVT ensemble, and the conformations of the molecule are stored every 10 fs, which leads to a trajectory file containing 100 conformations. Each conformation is then used as sorbate during a 1500-step fixed loading sorption simulation. Finally each host-guest configuration generated during the sorption is relaxed until the RMS force is lower than 0.02 kcal/mol/Å or the maximum number of minimization steps (1000) is achieved. With this set of parameters, the procedure duration is around 48 h. When the procedure is finished, the minimum interaction energies are calculated and the configuration with the lower energy is assumed to represent the most favored location of the coke molecule inside the pore structure of the zeolite.

3. RESULTS

3.1. Low-Temperature Coke

The coke molecules formed during toluene transformation at 120°C on H-MFI can be classified into two families resulting from the condensation of two or three toluene molecules, methyldiphenylmethane and methyltriphenylmethane. These molecules, which have a critical size similar to that of toluene molecules, may diffuse in the channels. Their retention in the zeolite pores was therefore proposed to be due to their low volatility (their boiling point, 265–380°C, is indeed much higher than the reaction temperature) and to their adsorption on the acid sites. A successive scheme was found for the formation of these coke molecules (1); see Scheme 1.

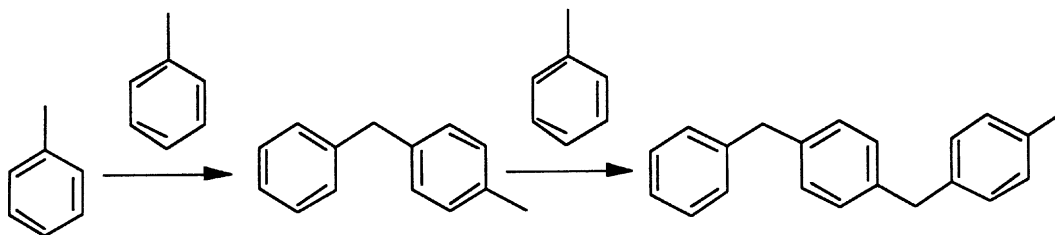
Location of methyldiphenylmethane isomers. There are three methyldiphenylmethane isomers differing by the position of the methyl group (Fig. 1). The starting point for the sorption procedure was chosen at the centre of the superlattice inside the straight channel as shown on Fig. 1-I. Figure 1-II represents the location of the three methyldiphenylmethane isomers after the sorption procedure (MC), and Fig. 1-III shows the minimum energy location for each isomer after complete energy minimization (RMS force ≤ 0.02 kcal/mol/Å). From Figs. 1-I to 1-III it can be observed that each coke molecule moves from the cen-

tre of the superlattice to a position where the phenyl group is located at the intersection between straight and zigzag channels. The values for the minimum energy location are very close to each other, but 4-methyldiphenylmethane is the most favored isomer.

Location of methyltriphenylmethane isomers. Considering that methyltriphenylmethane molecules result from the alkylation of methyldiphenylmethane molecules blocked inside the pore structure (1), the location of methyltriphenylmethane was researched using as starting point the more stabilized methyldiphenylmethane isomers, i.e., 4-methyldiphenylmethane. Six isomers can result from alkylation of this isomer according to the side of the channel from where the alkylation occurs and to the position of the methyl group. The lower interaction energy location for each isomer of methyltriphenylmethane is represented in Fig. 2. The more favourable location ($E_i = -40.8$ kcal mol⁻¹) corresponds to isomer (I) resulting from alkylation of 4-methyldiphenylmethane at a channel intersection by a toluene molecule located in a zigzag channel.

3.2. High-Temperature Coke

Trimethylpyrene isomers are the main components of the coke formed during toluene transformation at 450°C over H-MFI. Methylfluorene as well as traces of methylanthracene or phenanthrene are also detected (1). The location of nonsubstituted pyrene molecules was first determined. Pyrene is preferentially located at the intersection of the straight and the zigzag channels (minimum energy of -3.4 kcal mol⁻¹). In Fig. 3A, which represents the location of this molecule, the van der Waals volumes of Si and O atoms are represented, with their Connolly surface (grey) and the volume of the pyrene molecule given by the van der Waals radii of the atoms. To obtain a more clear view, only the intersection of the straight and the zigzag channels, where pyrene is trapped, is represented. The main direction of the pyrene is in the straight channel, and only one aperture (marked by a black arrow) of the two zigzag channels is occupied by pyrene. By considering this location, it can be concluded that only three hydrogen positions (marked in grey) can be substituted by methyl groups, which explains why no pyrene molecules with more than three methyl groups are found in coke (1). The



SCHEME 1

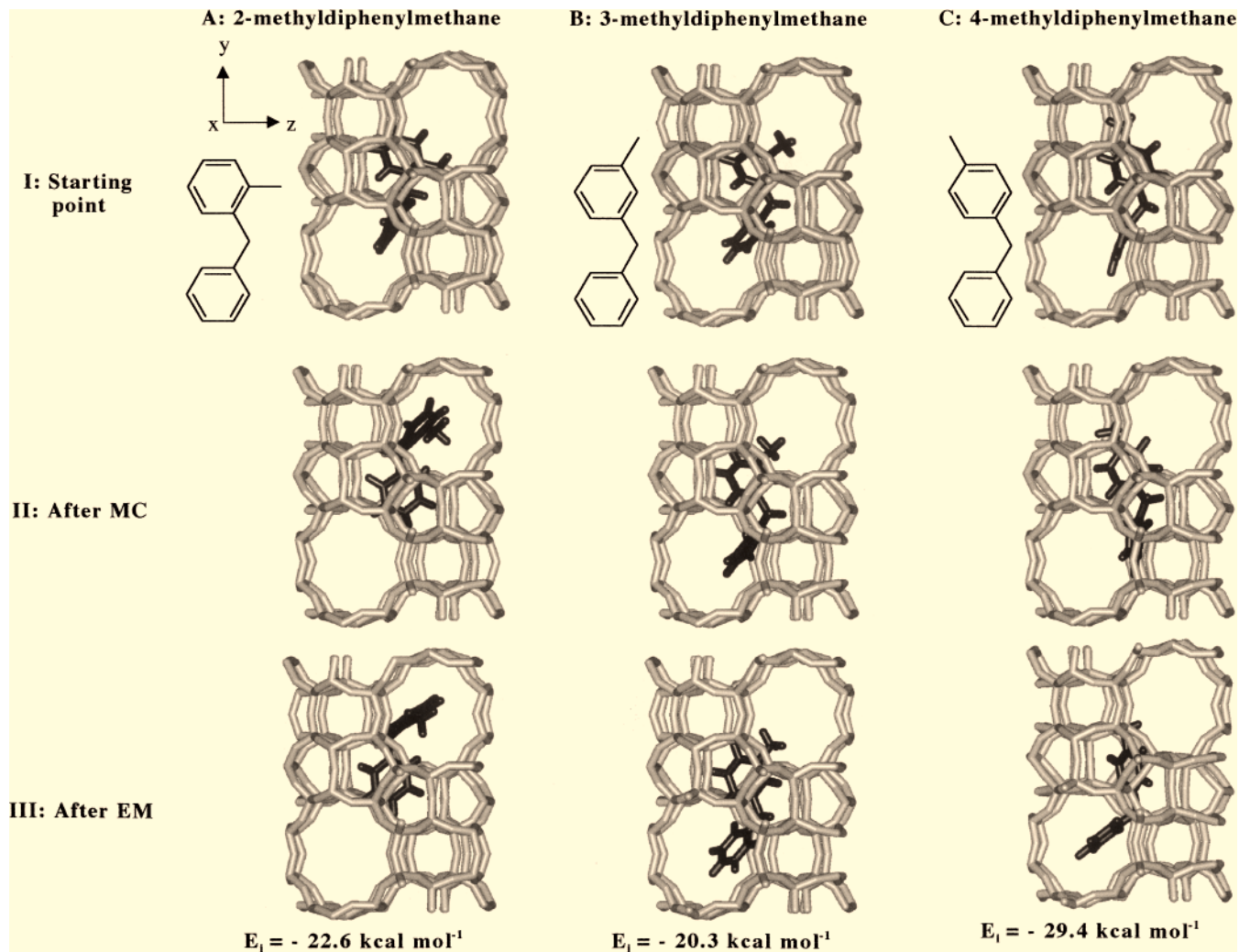


FIG. 1. Representation and interaction energy of the three isomers of methyldiphenylmethane. I, starting points inside the zeolite; II, after the Monte Carlo (MC) procedure; and III, after energy minimization (EM).

preferential location of the most favoured trimethylpyrene isomer is represented in Fig. 3B (the three methyl groups are marked in grey). It should be emphasized that the presence of the methyl groups stabilizes the pyrene inside the zeolite: the energy of the trimethylpyrene is more than four times lower than that of the pyrene.

4. DISCUSSION

The formation of coke requires not only reaction steps but also the retention of the resulting products: coke is a nondesorbed product. At low temperature the retention of coke molecules is often due to their low volatility. However, although the coke molecules formed during hydrocarbon transformation are generally not very basic, their adsorption on the protonic sites can also play a role by limiting their migration in the pores, hence their desorption of the zeolite crystallites. If, as is generally the case, the low

volatility of coke molecules is the main cause of their retention, these molecules can be located in various positions in the zeolite pores. Molecular modeling is the only way to determine their preferential location. This was done here for the coke molecules resulting from toluene transformation at 120°C over an H-MFI zeolite through an automated method adapted from the docking procedure first used by Freeman *et al.* (9).

The location of the three isomers of methyldiphenylmethane, which are the main coke components at a short time-on-stream, was determined. In all cases the minimum interaction energy is negative and no important zeolite framework deformation is observed, which proves that all these molecules can be formed inside the zeolite pores. For each isomer, a phenyl group is located at the intersection between the straight channel and a zigzag channel. This shows that the intersection stabilizes these dimers of toluene. It should be underlined that this position is also

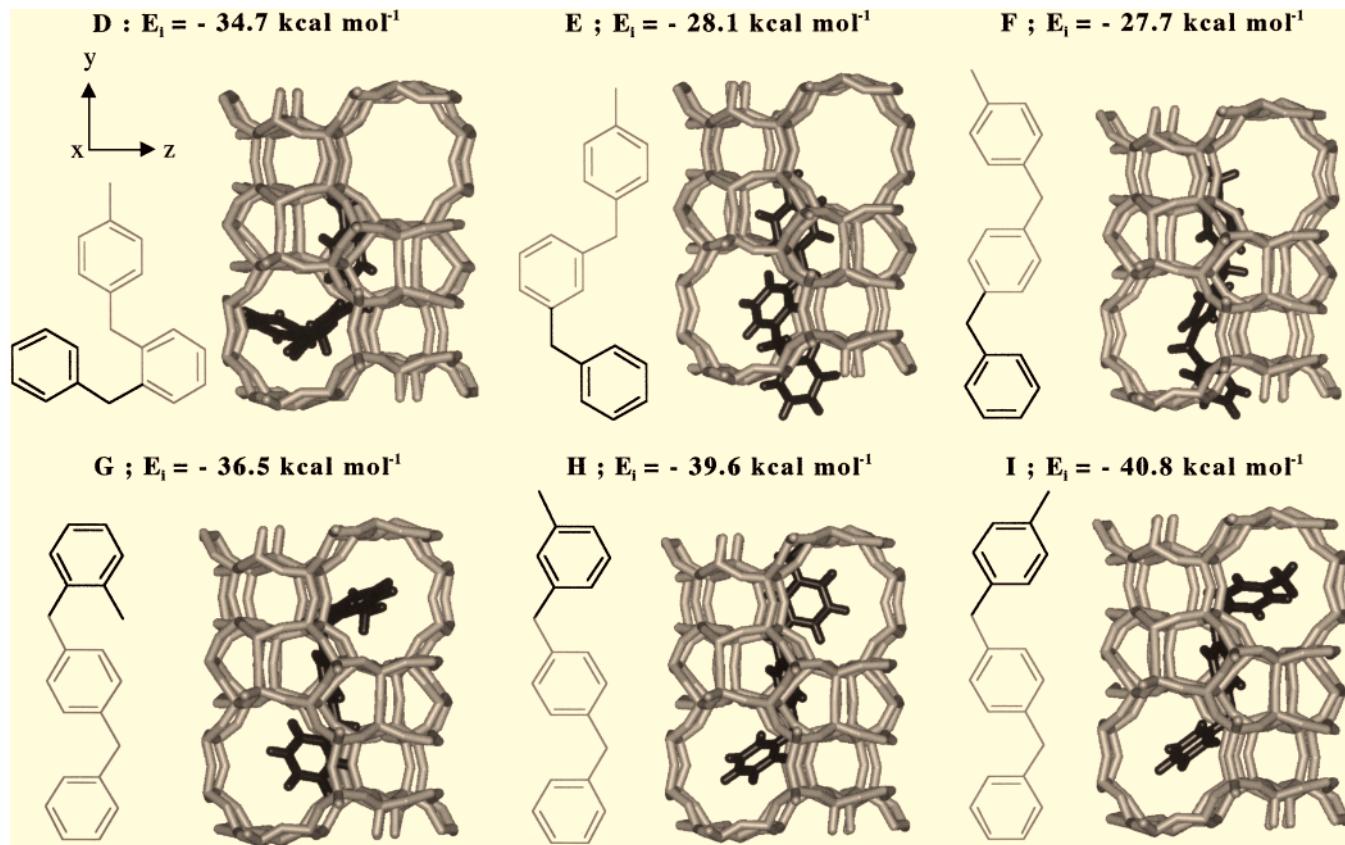


FIG. 2. Final location and interaction energy after energy minimization of the six isomers of methyltriphenylmethane. Isomers D to F result from alkylation of 4-methyldiphenylmethane (grey) by toluene (black) from the down side of the straight channel and isomers G to I from the high side of the straight channel.

necessarily that of the formation of dimers. Indeed it is generally admitted (19, 20) that the acid sites of H-MFI are located at channel intersections. Even if the energy values are very close to each other, the most favourable isomer is the 4-methyldiphenylmethane. It should be emphasized that methyldiphenylmethane is an intermediate in toluene disproportionation (21). With MFI zeolites a high selectivity to *p*-xylene is found, which is attributed to the fast diffusion of this smallest isomer inside the zeolite pores (100 times and 1000 times faster than *ortho* and *meta* isomers). This paper shows that transition state selectivity has also a positive effect on the formation of *p*-xylene. Indeed the intermediate of toluene disproportionation into *p*-xylene, i.e., 4-methyldiphenylmethane, is preferentially accommodated in the pore structure of MFI.

The location of methyltriphenylmethane isomers, which are the main components at a long time-on-stream, was determined by considering that these compounds result from the transformation of 4-methyldiphenylmethane. In contrast to the docking procedure implemented in the InsightII software, where the sorbate is randomly placed inside the zeolite lattice during the MC procedure, the method used here is very useful for following the growth of coke

molecules using as starting point a previously determined location.

At high temperatures the retention of coke molecules is due to their trapping in cages or channel intersections. Indeed their size is between that of cages or channel apertures. The first role of molecular modeling is therefore to compare these sizes on an accurate basis. However, as shown in this paper, for the coke molecules formed during toluene transformation over H-MFI at 450°C, molecular modeling leads to complementary information. Thus it was possible to explain by steric constraints why only pyrene molecules with three methyl groups at the maximum were found in coke. It was also shown that two methyl groups of the most favored trimethylpyrene coke component were located in the straight channel direction, the third one being located in one of the zigzag channels.

In the developed method it is possible to adjust the parameters of the procedure steps. Thus the number of conformations of the coke molecules generated during the NVT can be chosen. Here, because of the flexible structures of methyldiphenylmethane and methyltriphenylmethane molecules, a large number of conformations (100) was chosen. Figure 4A shows that this large number was necessary:

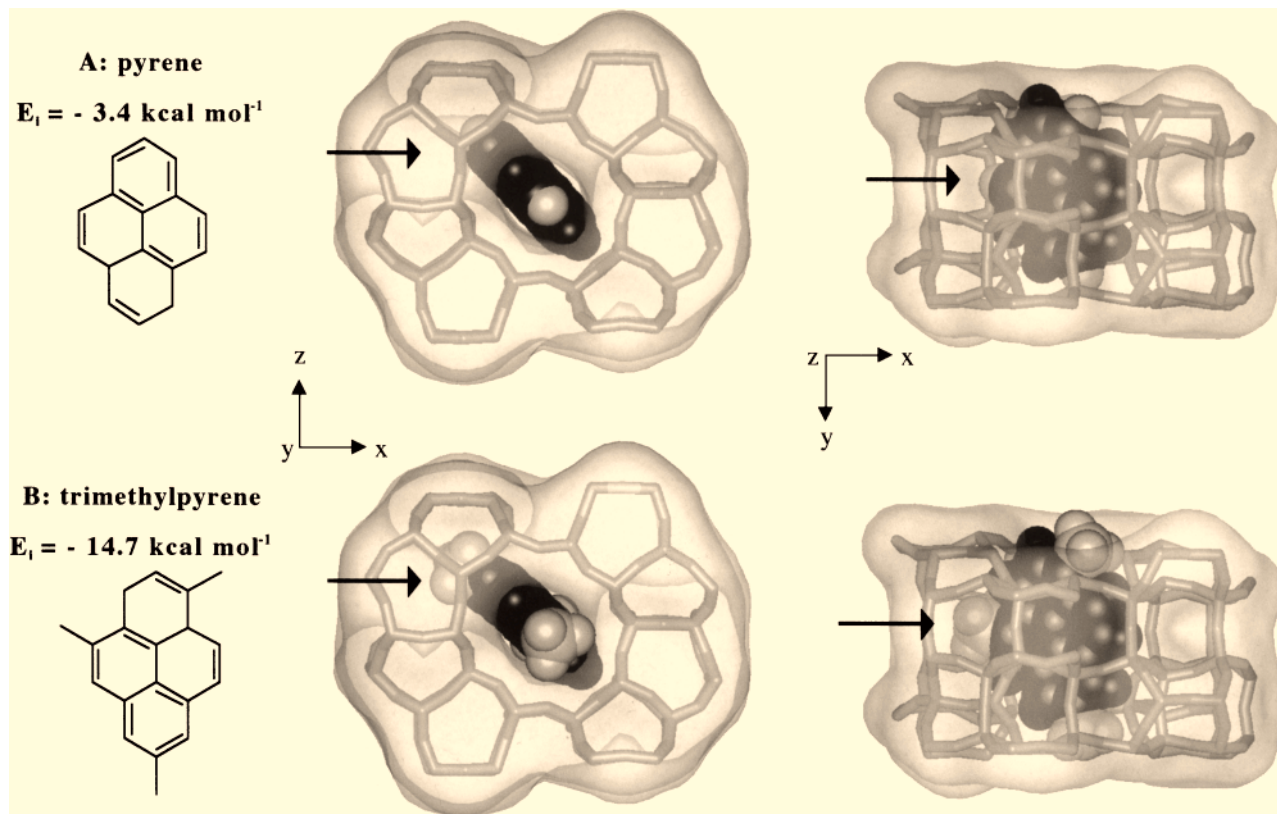


FIG. 3. Final location of the pyrene (3A) and of trimethylpyrene (3B) inside MFI channels (the arrows indicate the direction of one zigzag channel). The three hydrogen positions in grey (3A) are those which can be substituted by methyl groups, in grey (3B).

indeed, only 13% of the conformations present an energy close to the lower one. On the other hand, at high temperature the coke molecules, being polyaromatic, are less flexible, and the number of conformations generated dur-

ing the NVT can be lowered to decrease the computational cost. Indeed, with trimethylpyrene, 48 of the 100 conformations (Fig. 4B) present an energy close to the lower one. Therefore the number of conformations can be decreased

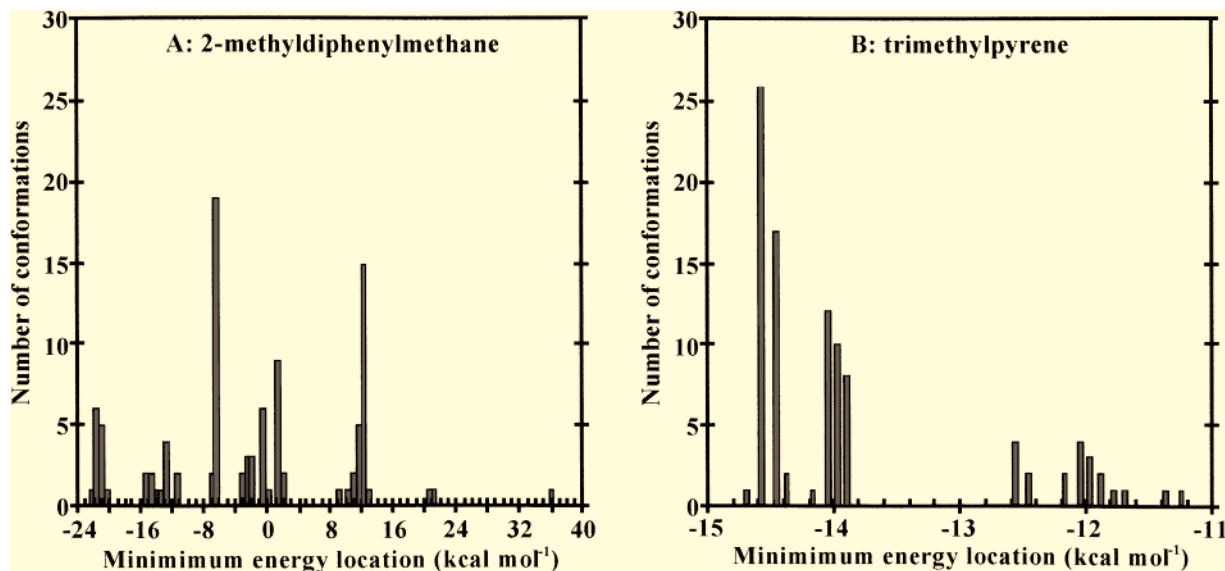


FIG. 4. Distributions of the interaction energy in the case of a flexible coke molecule (A, 2-methyldiphenylmethane) and of a rigid coke molecule (B, trimethylpyrene). In each case the total number of conformations is 100.

for high-temperature coke molecules, with consequently a decrease in the computational time.

5. CONCLUSION

An automated molecular modeling method was developed to locate coke molecules and to follow their growth inside zeolite pores. This method, adapted from that previously developed by Freeman *et al.* (9), is based on the consecutive use of isothermal molecular dynamic (NVT), Monte Carlo simulation (sorption), and energy minimization procedures. The automation is obtained using the scripting capacity of the Cerius2 software combined with the Tool command language (Tcl). The results, obtained on the location of coke molecules formed during toluene transformation at low and high temperatures, demonstrate the interest of the method.

At low temperature, all the coke molecules, methyl-diphenylmethane or methyltriphenylmethane, were preferentially located at the intersections between the straight channel and the zigzag channels. Moreover, the sorption procedure used here allows us to orient the choice of the starting point. This feature is useful for following the growth of coke molecules blocked inside the zeolite.

Pyrene molecules, which are the main components of high-temperature coke, are shown to be only located at the intersection between the straight channel and one zigzag channel. Furthermore, in agreement with the coke composition, it is shown that due to steric hindrance, pyrene molecules can bear three methyl groups at the maximum, two being located in the straight channel direction and the third one being located in one of the zigzag channels.

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