

Diffusion of hydrocarbons in the reforming catalyst: molecular modelling

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Abstract

This is an analysis of the diffusion and adsorption of the model reagents involved in the reforming process (heptane, methylcyclohexane and toluene) in the support (γ - Al_2O_3) and catalyst (Pt/γ - Al_2O_3) made use of in this process. Since the properties of these catalytic systems are influenced by the interactions between the atoms of the catalyst structure (host) and the atoms of the reagents (guest), analysis was carried out at the molecular level, using advanced computer simulations (molecular dynamics and forced diffusion) implemented in the MSI Software. The virtual host–guest model constructed with this software enabled a simulation of the real reforming system (reforming catalyst–reagents) and analysis of the diffusion phenomenon in this system.

The results show that the propensity of the reagents to adsorption and the host–guest interaction energy are correlated with the coefficients of diffusion. The diffusion coefficient values are lower in the catalyst than in the support, probably because of the increased adsorption at the active Pt centres. The decrease in pore diameter from 17 to 10 Å brings about a decrease in the diffusion coefficients not only due to steric hindrance, but also as a result of capillary condensation. The favourable influence of temperature is more distinct in models characterised by a larger pore size. This is so because molecular diffusion dominates over the mechanism of Knudsen diffusion, which increases the temperature-dependence of diffusion.

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1. Introduction

The objective of catalytic reforming is to produce high-octane petrol by increasing the content of aromatic compounds and ramified *iso*-paraffins in the feed with dominating *n*-paraffins and naphthenes. The kinetics of the process and the reactions involved, as described by Froment and co-workers [1–5], are sophisticated. In the course of the process, paraffins dehydrocyclise to naphthenes which, in turn, convert to aromatic compounds, whereas *n*-paraffins isomerise to form *iso*-paraffins. The undesired reactions of hydrocracking convert some part of the product into light paraffins. There is a substantial difference in the rate between particular reactions. Thus, the hydrogenation of naphthenes to aromatic hydrocarbons runs at a rate which is by two orders of magnitude faster than the rate with which paraffins are dehydrocyclised to naphthenes. Hence, under the same process conditions, slower reactions may run in the kinetic region whereas faster reactions may be constrained by diffusion resistance, thus slowing down the rate of the process.

Owing to the various rates of the reactions involved, the overall rate of the process is affected by the rate with which the reactants and the products are transported inside the grain of the catalyst. Thus, the problem of hydrocarbons diffusion in the catalyst has taken on a sense of importance (both theoretical and practical), especially in such cases where the diffusion rate determines the overall rate of the reforming process. This is so whenever the free space in the micropores of the catalyst is comparable to the size of the diffusing molecules, which may impair the transport of the reagents. Our knowledge of how the catalyst works is generally far from being comprehensive. On the other hand, it is necessary to know the energetically preferred sites, as well as the interaction energy and the diffusive capabilities of the organic guest molecules inside the pores and channels of microporous solids (catalysts), if we want to understand the sorptive and catalytic behaviour of such materials. The properties of catalytic systems (activity, selectivity) are strongly influenced by the interaction between host and guest molecules. Hence, in order to understand the nature of such processes we need to analyse these interactions at the molecular level. Combined with the sophisticated methods of computer simulations, such analysis may provide information about the properties (catalytic and adsorbing) that owe their origin to

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the host–guest interaction but are difficult to reveal by experiments only. Host–guest interactions are of crucial importance when determining the diffusive properties of hydrocarbons in the micropores of the catalyst [6].

Many experimental methods are available for the determination of the diffusion coefficients. In general, they can be divided into macroscopic and microscopic [7]. In the macroscopic methods, the dynamic response of a small catalyst sample is related to flow rate disturbances or sorbate concentration variations. Microscopic methods enable the mean square displacement of the guest molecules to be assessed under equilibrium conditions.

Recently, molecular simulation has received acceptance as a convenient tool which can be used to investigate the host–guest system. Molecular simulation makes it possible to construct a model of the investigated system and to generate the behaviour of a real system. With such method it is possible to study the dynamics and the diffusive properties of catalytic systems. Some recent studies where use was made of computer simulations deal with the diffusion of small molecules in zeolites. In contrast to many heterogeneous catalysts, zeolites are well characterised crystalline materials. Their surface is available to the reactants and their active sites are well defined. Because of this, molecular simulation seems to be well suited for application in such cases. Of the frequently simulated systems, methane in silicate has come to the forefront [8,9]. Goodbody et al. [10] have simulated the molecular dynamics for methane in silicate in order to relate the diffusion coefficients to the number of guest molecules in an elementary cell. Bouyernaouen and Bellemans [11] have proposed two different simulations of *n*-butane and *i*-butane in silicate. In one of these they have assumed that the crystal structure of silicate is rigid; in the other they have allowed it to be flexible. They have found that lattice vibrations produce changes in the size of the micropores, thus making diffusion easier. Tsekov and Ruckenstein [12] have related the diffusion coefficients of paraffins in the T-zeolite to the length of the carbon chain.

The results of computer simulations made use of in the assessments of the diffusion coefficients for zeolites are easy to verify by experiments. The better is the agreement between the simulated and experimental values, the more reliable is the computational model. The term ‘computational model’ has been used to denote both the method with which the atomic interactions have been described and the method with which the simulation has been carried out.

Unlike the computer-simulated results for zeolites, those for the reforming catalyst model are difficult to verify due to the disordered structure of the alumina oxide used as catalyst support. This disorder is to be attributed to lattice defects, as well as to the presence of a great number of micro- and macropores differing in shape and size. That is probably why no molecular simulations have been applied to aluminum oxide as a support for the reforming catalyst. Specialized literature contains many references to the porous structures of a variety of catalysts—from monodispersive [13] through

bidispersive [14–16], to models including a wide range of pore distribution [17]. A chronological review of such models (from the simple Wheeler model to the models developed in the 1990s) can be found elsewhere [18,19].

The aim of the present study was to propose a simplified computational model. With this model it is possible to evaluate the contribution of the pore size, as well as that of the Pt atoms which are present in the host structure (γ -Al₂O₃), to the diffusivity of the hydrocarbons in the reforming catalyst. The physical model of the Pt/ γ -Al₂O₃ catalyst, the models of alkanes, naphthenes and arenes (heptane, methylcyclohexane and toluene), representative of the reactants involved in the reforming process, as well as relevant simulations and visualisations, were carried out with the MSI Software (Cerius² and Insight II) [20,21].

2. Model and computational details

Two approaches to the simulation of diffusion were used in this study—forced diffusion and molecular dynamics, which should be considered as complementary methods. The use of molecular dynamics provides information on such properties of the system as the diffusion coefficients and makes it possible to relate them to temperature, pressure and pore size or to the presence of heteroatoms in the host lattice. Owing to the internal dynamics of the molecule, we can get insight into the free (unrestricted) pathway of molecule motion. Forced diffusion offers the possibility to estimate the location and height of the energetic barriers on an arbitrarily chosen path of the guest molecule.

In order to obtain reliable results the following has been assumed:

1. The micropores were created by deleting selected atoms from bulk crystal in order to make them connect the centres of two opposite cell sides. The direction of micropores has been set to [100] (note that [010] and [001] directions are identical due to symmetry).
2. The simulation of molecular dynamics needs two models—one with a pore diameter of 10 Å, the other one with a pore diameter of 17 Å, as in this way it is possible to establish the relationship between the coefficients of diffusion and the size of the micropores. The results obtained with a single simulation that involves a model where micropore size or shape is varied are difficult to interpret, so the information provided via this route might not be reliable.
3. For the simulation of forced diffusion it suffices to use one model with varied micropore size—10 Å diameter in the narrow part and 17 Å diameter in the wide part (Figs. 1–3). In a sense, this model is a combination of the two models prepared for the molecular dynamics. When simulation is carried out under such conditions, we can estimate the height of the energetic barrier produced by the changing size of the micropores. Such estimation would not be feasible if the simulation involved

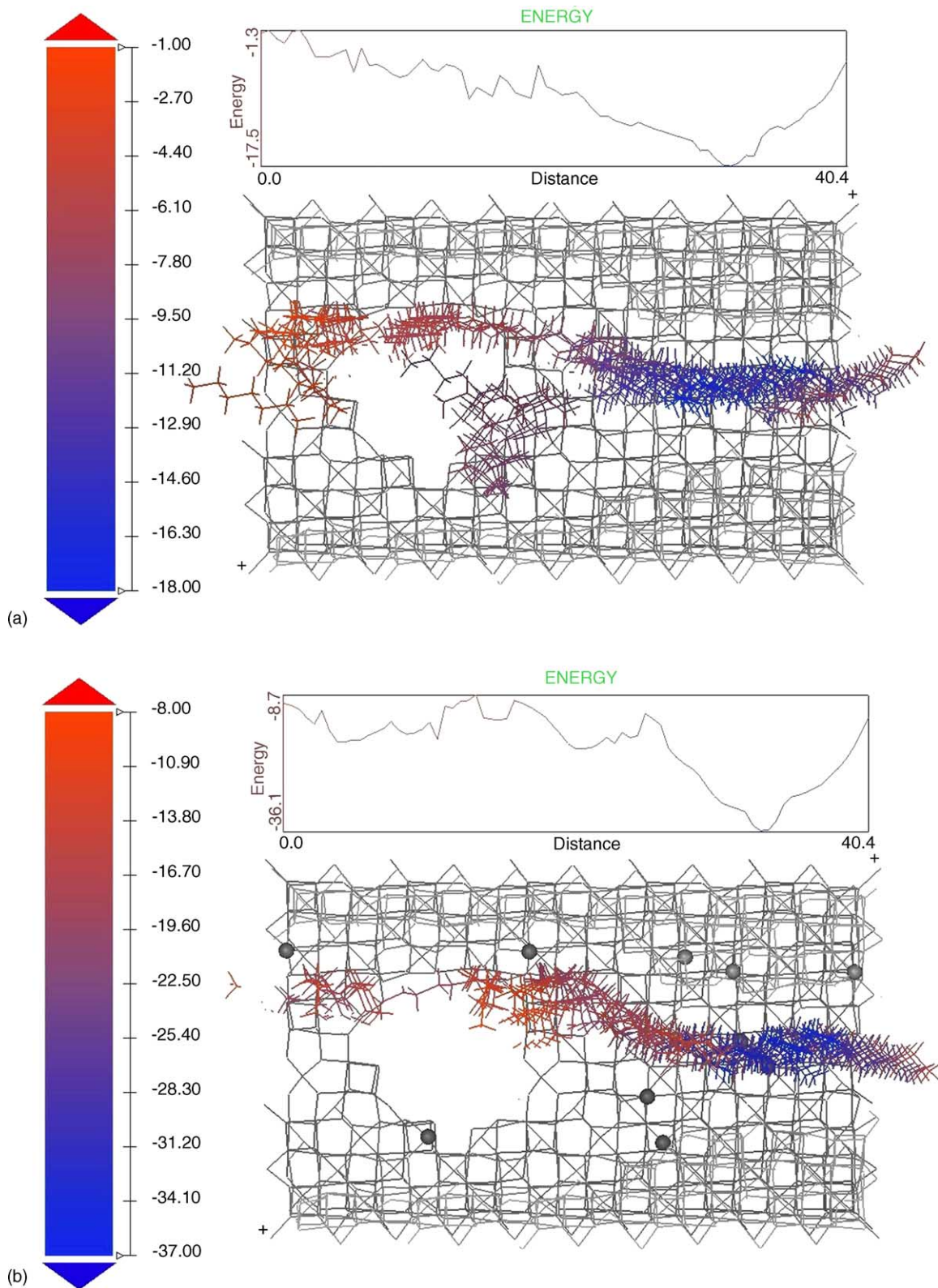


Fig. 1. Minimum energy paths for heptane in Al_2O_3 (a) and $\text{Pt}/\text{Al}_2\text{O}_3$ (b). Color of molecule represents interaction energy.

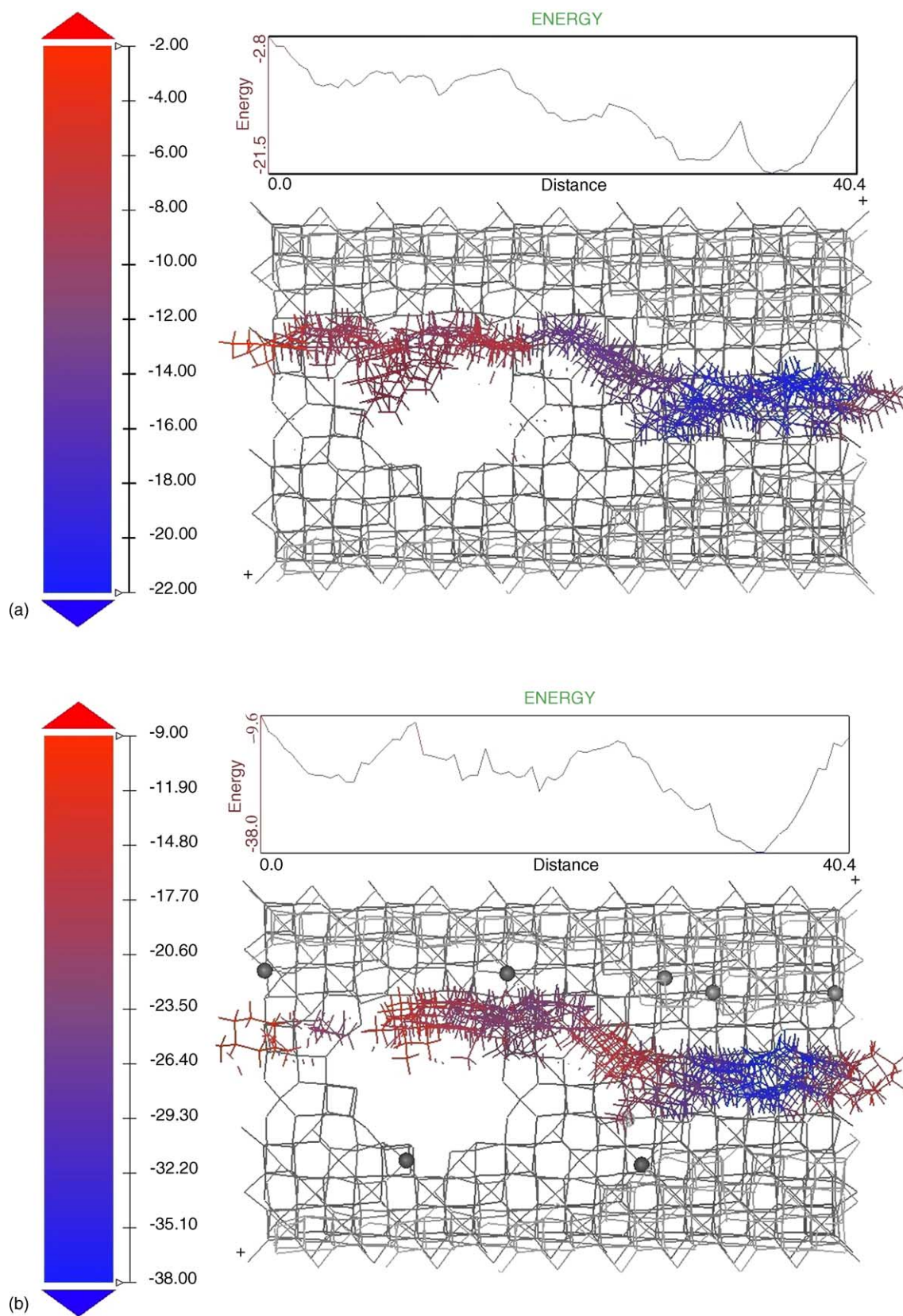


Fig. 2. Minimum energy paths for methylcyclohexane in Al_2O_3 (a) and $\text{Pt}/\text{Al}_2\text{O}_3$ (b). Color of molecule represents interaction energy.

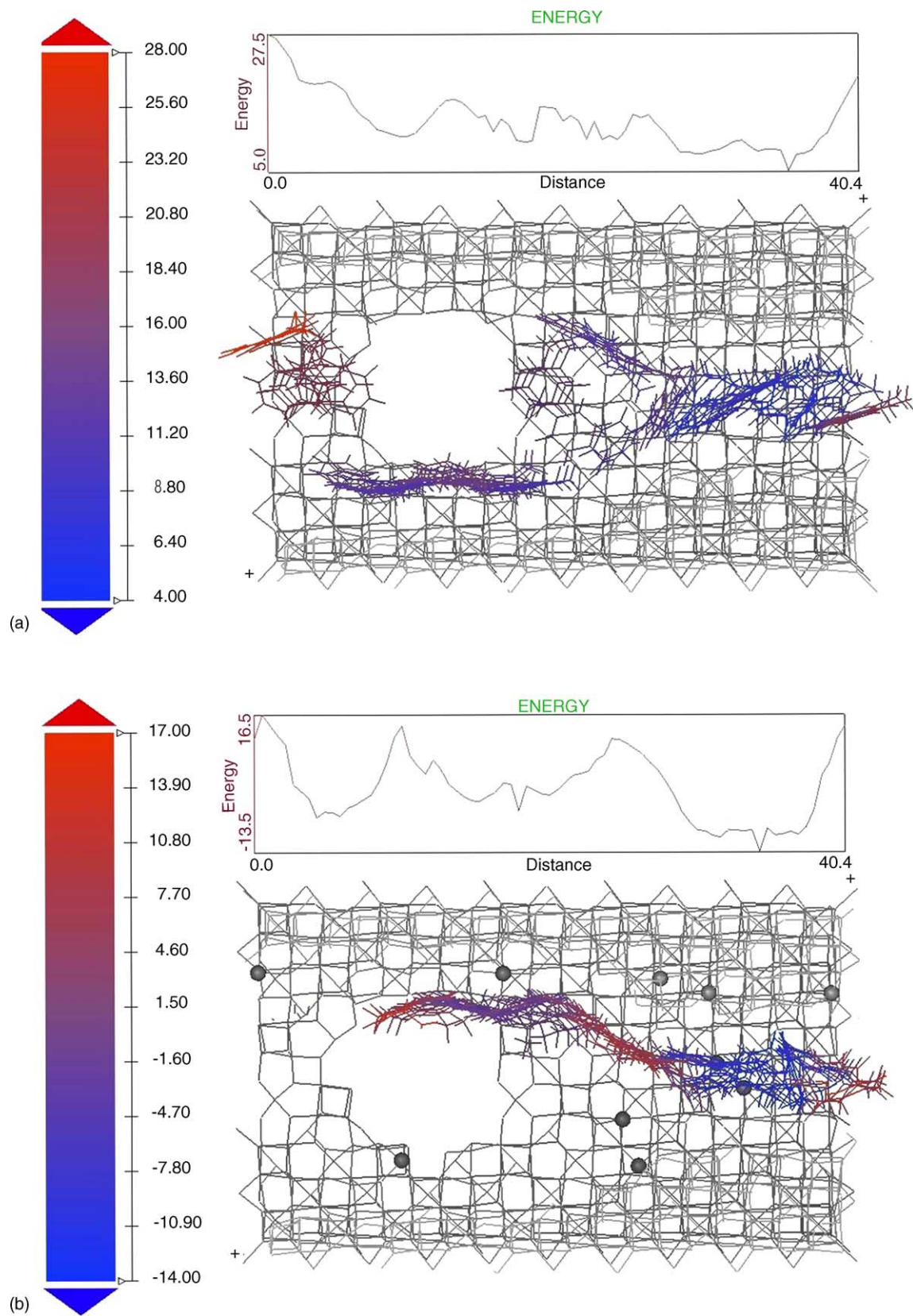


Fig. 3. Minimum energy paths for toluene in Al_2O_3 (a) and $\text{Pt}/\text{Al}_2\text{O}_3$ (b). Color of molecule represents interaction energy.

models of two constant diameters, as those for the molecular dynamics. These models suggest the occurrence of energetic barriers produced only by the difference in the mean energies of the interactions between the diffusing molecules and the γ -Al₂O₃ structure as a function of the site of the diffusing sorbate.

4. Pt-containing models can be built by substituting the Al atoms on the surface of the micropore with noble metal atoms. Pt is not likely to occur in the bulk crystal, but predominantly on the pore surface. Since the only difference between models is the presence of the foreign metal, the change in the energy of interaction cannot be affected by any other factors. The noble metal is attached to the surface by the bridging oxygens, hence its oxidation state is +4 [22].
5. Since the size of the Pt particles depends on the preparation technique used, we have arbitrarily assumed its maximal dispersion. Models prepared in this way contained more Pt centres located along the molecule's path. Compared to the real catalyst, the content of platinum would be too high if larger metallic particles were applied.
6. To simulate the diffusion of particular hydrocarbons, use can be made of the same models. In this way it is possible to eliminate the influence of some undesired factors (e.g. that of the different Pt atom positions in the host model).
7. The presence of hydroxyl groups in the host structure has been neglected. Although the surface energy of alumina is temperature-dependent, in the model with a hydroxyl coverage of 14.8 it is equivalent to a fully dehydrated surface in 773 K (reforming conditions) [23], hence the assumption that it has no effect on the host–guest interactions.

It has to be noted that none of these models can be regarded as a simplified model of a real system, but only as a part of it. The structure of the catalyst is not that of a monocrystal, and does not consist of identical cells. However, if we treat a single γ -Al₂O₃ model as a small part of a real structure, we can gain a better understanding of the phenomena occurring in particular fragments of the system, e.g. how the shape and the size of the single micropore, as well as the presence of Pt atoms, affect the diffusion of hydrocarbons.

To determine the energy of the system, use was made of the Consistent Valence Force-Field (CVFF) [24–31], with following Pt parameters: $A_i = 4576819.9618$, $B_i = 16963.30818$ [32].

Host structure was held rigid during the simulation. Such assumption is likely to propagate errors, especially when the diffusing hydrocarbon is 'tightly set' in the micropore, because the oscillations of the sorbent facilitate motion [11]. Needless to say that the calculating costs would rise dramatically.

The γ -Al₂O₃ models were constructed using the atom coordinates from the Cerius² database [33]. Before starting the simulations, the geometries of the models were optimised.

2.1. Forced diffusion

The γ -Al₂O₃ support model selected for simulation was made of 80 ($4 \times 4 \times 5$) unit cells. The micropore was cylindrical in shape and its diameter changed at half length from 10 to 17 Å (Figs. 1–3). The simulation procedure was repeated with the Pt/ γ -Al₂O₃ catalyst model which had been constructed on the basis of the support model by substituting Al atoms with Pt atoms so as to obtain the Pt content of a real catalyst. The model contained 17 Pt atoms attached to the micropore surface through the bridging oxygens. Calculations were carried out according to the forced-diffusion procedure implemented in the Solids_diffusion module of Insight II [34].

The hydrocarbon molecule was forced along an arbitrarily chosen path with regular steps of 0.5 Å. The computational process involved several optimisations of the system geometry, the starting point being the position of the diffusing hydrocarbon molecule in successive steps. The diffusion pathway was determined by establishing its starting and ending points.

The simulation of forced diffusion yielded curves (Figs. 1–3) where the energy of the sorbent–adsorbate interaction is related to the position of the diffusing sorbent. Practically, the minimum energy pathway (MEP) shows the deviations of the interaction energy along a selected path of sorbent diffusion in the adsorbate and can be used to define the position and height of the energetic barrier which impairs the movement of the sorbent.

2.1.1. Results of forced diffusion simulation

Figs. 1–3 show the MEP for heptane, methylcyclohexane and toluene molecules travelling along the z -axis in the models of γ -Al₂O₃. The values of the interaction energies depend on the size of the micropore and on the distance of the molecule from the Pt centre. As shown by the plots, the energy of interactions decreases with the decreasing micropore diameter and becomes negative for each guest molecule. Decreased energy values substantiate the occurrence of adsorption, which increases as energy decreases to produce the immobilisation of the molecule. Thus, the decrease in the diffusion coefficients should be attributed not only to steric hindrance but also to the immobilisation of the molecules as a result of stronger adsorption or potential condensation.

However, adsorption and steric effects cannot be regarded as the only factors that affect the diffusion coefficient values. While the host–guest interaction energy for heptane and methylcyclohexane is comparable (Figs. 1 and 2), the values of the diffusion coefficients (D) for heptane are six times higher than those for methylcyclohexane (Tables 1 and 2). This difference is likely to be contributed by the flexible chain structure of heptane and the rigid ring of methylcyclohexane.

What accounts for the decrease in the interaction energy is also the presence of the Pt centres (Figs. 1b, 2b and 3b). Like narrow micropores, platinum facilitates the adsorption

Table 1
Diffusion coefficients for hydrocarbons in models of catalysts in [$\text{\AA}^2/\text{ps}$]

T (K)	10 \AA micropore			17 \AA micropore		
	Heptane	Methylcyclohexane	Toluene	Heptane	Methylcyclohexane	Toluene
500	8.132E–03	2.620E–03	6.838E–03	5.286E–02	2.558E–02	9.762E–03
700	3.028E–02	6.166E–03	2.10E–02	1.348E–01	1.009E–01	1.104E–01
900	4.220E–02	6.775E–03	1.118E–01	6.451E–01	3.164E–01	4.015E–01

Table 2
Diffusion coefficients for hydrocarbons in models of catalysts supports in [$\text{\AA}^2/\text{ps}$]

T (K)	10 \AA micropore			17 \AA micropore		
	Heptane	Methylcyclohexane	Toluene	Heptane	Methylcyclohexane	Toluene
500	8.959E–03	5.099E–03	5.875E–02	1.613E–01	3.682E–02	3.707E–01
700	3.073E–02	7.948E–03	1.437E–01	2.634E–01	3.429E–01	9.951E–01
900	5.371E–02	2.862E–02	1.943E–01	8.533E–01	1.376E+00	1.091E+00

of hydrocarbons to the surface of $\gamma\text{-Al}_2\text{O}_3$. For each guest molecule the interaction energy in the vicinity of the Pt centre decreases by approximately 20 kcal/mol. The difference in the interaction energy between the models with and without platinum is the smallest for heptane (Fig. 1a and b), and so is the difference in the diffusion coefficients for this hydrocarbon. Toluene follows a similar pattern—the interaction energy is much lower near the Pt centre and so is the diffusion coefficient as compared to the model where Pt is absent (Tables 1 and 2).

2.2. Molecular dynamics

Simulation was carried out with four models built of cylindrical micropores. Two had a diameter of 10 \AA (with and without Pt) and were constructed from 27 elementary cells ($3 \times 3 \times 3$). The other two, with a diameter of 17 \AA , were made of 64 cells ($4 \times 4 \times 4$). The system was assumed to be an infinite one by the adoption of periodic boundary conditions. The system can be regarded as a crystal (a single supercell) with an infinite number of micropores arranged in parallel to one another, such as the one used in a previous study [16]. The dimensions of the models were chosen so as to prevent any influence of the parallel pores on the behavior of the diffusing molecule.

Molecular dynamics (MD) is amongst the most frequently used methods of simulation. It makes use of the internal dynamics of the molecule to calculate the forces acting on the atoms. MD is carried out according to the computational algorithm of finite steps [35]: in each time step (t), using the calculated values of the forces and the positions of the molecules which have been established in the preceding step, the new position and momentum of each molecule are calculated by solving numerically the Newton equation of motion [36]. With the computed forces and the displacement of the atoms it is possible to assess the trajectory of motion for the molecule. The plot of the mean square dis-

placement (MSD) function versus time enables the diffusion coefficient of the adsorbate to be calculated.

All simulations were carried out in the NVT ensemble with the Damping thermostat [37]. The total time of the simulations was set to 100 ps for the equilibrium run and 400 ps for the data collecting run. The time step was set to 1 fs. The guest molecules were the same as in the simulation of forced diffusion. Under these conditions, single molecules of heptane, *iso*-heptane, methylcyclohexane and toluene in the $\gamma\text{-Al}_2\text{O}_3$ model and Pt/ $\gamma\text{-Al}_2\text{O}_3$ model were simulated. The simulations were repeated for the temperatures of 500, 700 and 900 K. The diffusion coefficients were obtained by determining the slope of the MSD curve with time. It was assumed that the simulation would last long enough so that the observed motion of the molecule would really be diffusive in nature.

2.2.1. Results of MD simulations

The calculated values of the diffusion coefficients are gathered in Tables 1 and 2. As shown by these data, the increase in the values of the diffusion coefficients can be attributed to the increased micropore size, to the rise in temperature and to the removal of the Pt atoms from the catalyst model (the latter contributing factor does not seem very convincing). According to expectations, the values of the diffusion coefficient rose when the micropore diameter increased from 10 to 17 \AA (Tables 1 and 2). This indicates that in the pore radius range mentioned the mechanism of molecular diffusion dominates over the Knudsen mechanism. With wider pores the effect of steric hindrance on molecule motion is not so strong, and the molecules have a greater freedom to move. The favourable influence of the increased pore radii on the values of the diffusion coefficients can be seen at each temperature for each of the investigated hydrocarbons diffusing either in the $\gamma\text{-Al}_2\text{O}_3$ support or in the Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalyst model. The positive effect of temperature is more distinct in models with larger micropores (Figs. 4b and 5b)

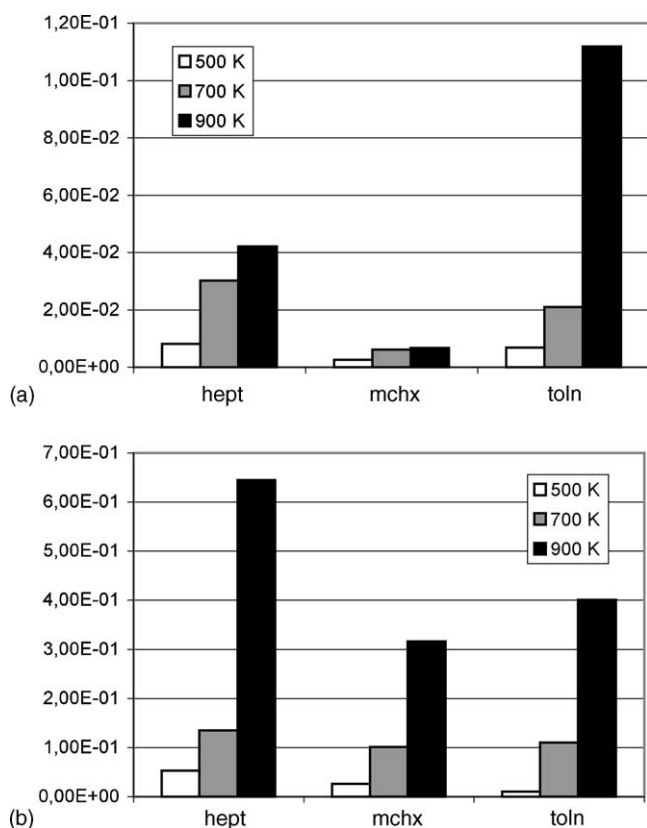


Fig. 4. Influence of temperature on diffusion coefficients: diffusion coefficients of hydrocarbons in Pt/Al₂O₃ model with narrow (a) and wide (b) micropore.

where the mechanism of molecular diffusion prevails over Knudsen's mechanism.

The explanation for the lower diffusion coefficients of all the hydrocarbons in the platinum-containing catalyst model (Tables 1 and 2) can be found in the analysis of the results obtained from the simulation of forced diffusion. From the MEP plots for forced diffusion it may be inferred that the presence of the Pt centres decreases the energy of the catalyst–guest molecule interaction. As a result, the adsorption in the proximity of the Pt centres is stronger, so the guest molecules become immobilised. The comparatively high diffusion coefficients of toluene (Tables 1 and 2) are likely to be the result of the increased energy of the host–guest interaction and, consequently, of the weaker adsorption, which may impair diffusion. The diffusion resistance in the small pores of the hydrocarbons with negative values of the host–guest interaction energy (Figs. 4a and 5a) can be attributed not only to steric hindrance but also to stronger adsorption. In such instances, it is not advisable to neglect the displacement of the molecules adsorbed on the surface of the adsorbent. It should be anticipated that the mechanism of surface diffusion (which plays an important role in the processes involved in polymolecular adsorption) might be acceptable. The mechanism of transport requires a significant amount of activation energy (up to 90% of the adsorption heat) and

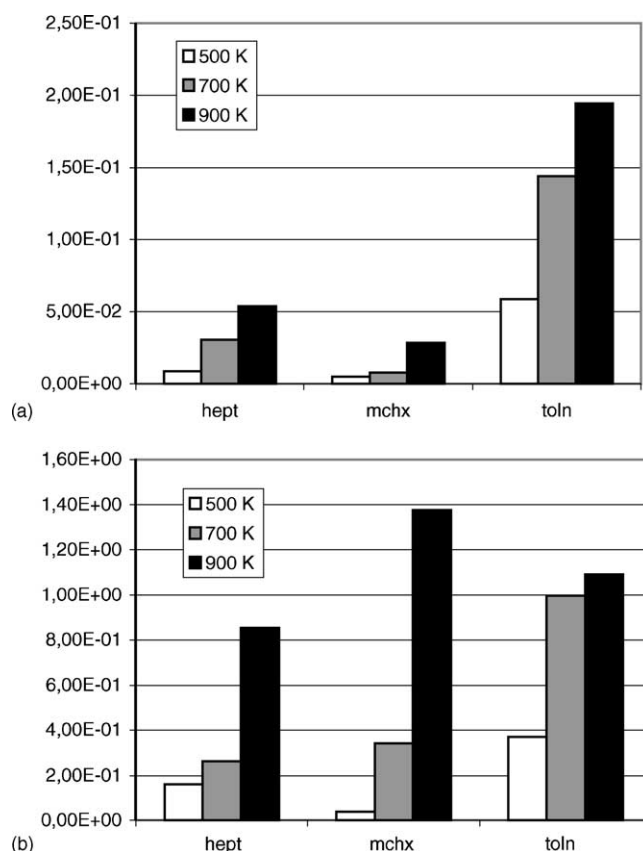


Fig. 5. Influence of temperature on diffusion coefficients: diffusion coefficients of hydrocarbons in Al₂O₃ model with narrow (a) and wide (b) micropore.

for this reason may be of little importance in real catalytic processes.

3. Conclusions

The methods dealt with in molecular mechanics (and the algorithms implemented in the MSI Software) were used to analyse the diffusion phenomena in the γ -Al₂O₃ support model and in the Pt/ γ -Al₂O₃ model of the reforming catalyst. The results obtained are found to be interesting and promising. They have revealed that the diffusion phenomenon and the adsorption of hydrocarbons on the walls of the support must not be studied separately. Besides steric hindrance, adsorption is one of the key factors that contribute to the diffusivity of the molecules. The negative (though comparable) values of the host–guests interaction energies for heptane and methylcyclohexane suggest that these two species have developed a greater propensity to adsorption than has toluene. The increased values of the diffusion coefficient for heptane should be attributed to the flexibility of the carbon chain. Furthermore, there is a difference in the diffusion coefficients between toluene and methylcyclohexane; although both the species could be regarded as rigid, the coefficient of diffusion for toluene is higher.

This difference may link up with the weaker tendency of toluene to adsorption (higher energy of interaction between the guest molecule and the host structure). In the support models (γ -Al₂O₃), where all of the diffusion coefficients are increased because of a weaker adsorption, the diffusion coefficients of toluene are even higher than those of heptane. This should be ascribed to the increased predisposition of the toluene molecules towards desorption and repulsion from the walls of the micropores at the moment of heptane adsorption. The influence of the micropore diameter on the diffusivity of the hydrocarbons suggests that the diffusion of hydrocarbons in the reforming catalyst follows the principles of the molecular and Knudsen's mechanisms. The strong adsorption of heptane and methylcyclohexane, especially in narrow micropores, points also to the mechanism of surface diffusion.

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