

Adsorption equilibria of hydrocarbons in the structure of the reforming catalyst: Molecular modeling

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Abstract

Molecular modeling was used to analyze the phenomena involved in the sorption of hydrocarbons by the Pt/Al₂O₃ reforming catalyst. The interactions between the atoms of the catalyst structure and the molecules of the model reforming compounds were described in terms of the universal forcefield. Making use of the GCMC algorithms, the adsorption isotherms for the reagents in the catalytic system and the temperature dependence of the Henry constant were determined. The research has produced the following major findings: the amount of the hydrocarbon molecules adsorbed rises with increasing pressure and decreasing temperature, and the adsorption isotherm for toluene has a characteristic plot as compared to the isotherms of the other hydrocarbons studied. Mass cloud analysis has revealed a favorable effect of platinum on adsorption in the catalyst model.
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1. Introduction

The majority of chemical processes are carried out in the presence of catalyst, but the way in which the catalyst acts has not yet been fully explained. The knowledge of the energetically advantageous positions, as well as of the interaction energies and potential diffusion of organic molecules in the structure and channels of microporous solids, is a prerequisite to understand the catalytic and ‘adsorptive’ behavior of such materials. The past decade has witnessed the development of many sophisticated computer-aided computational methods which could be of help in gaining such knowledge. The information obtained with these tools makes it possible not only to interpret the experimental results but also to gain insight into such properties of a catalytic-adsorptive system that would never be detected by experiments alone. Since the properties of a catalytic system (activity, selectivity) depend on the interactions between the atoms of the catalyst structure and the atoms of the reagents, we shall have to analyze the phenomena occurring in the catalyst at the molecular level if we want to gain reliable information about the nature of

catalytic processes. To model catalysts, it is conventional to use various techniques of simulation at the atomic level.

Forcefield-based methods (molecular mechanics) are used to model the structure of the catalyst, as well as the sorption and diffusion phenomena occurring in them, while the more accurate quantum mechanics methods are of utility in modeling the mechanisms of the reaction. A detailed description of the available molecular modeling methods can be found elsewhere [1–3].

The use of molecular modeling has become increasingly frequent recently. The understanding of the physicochemical phenomena that occur in the catalyst structure is a key issue in predicting the catalytic behavior of these materials. Molecular modeling visualizes any changes in the properties of the catalytic system as a result of the interaction between host and guest atoms. Our knowledge gained from the simulation of the adsorption and diffusion phenomena in the catalyst structure allows us to design new catalysts for particular processes we are interested in or upgrade the performance of the catalysts which are in use now by modifying their structures.

2. Aim and scope of the study

This study is the furtherance of our previous research into the physicochemical phenomena in the structure of the reforming catalyst, as well as in the support, at the atomic

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level. While our earlier study concentrated on the occurrence of diffusion phenomena and the location of active sites in the catalyst [4,5], the investigations reported on in this paper were focused on the adsorption equilibrium between the adsorbent (support and reforming catalyst Pt/ γ -Al₂O₃) and the adsorbate (model substrates of the process). In the study use was made of the molecular modeling (molecular mechanics) methods to investigate the sorption phenomenon in the host–guest system. Since references to the analysis of the said system by the molecular modeling method are lacking in specialized literature, our present research (as well as the previous ones) may contribute to a better understanding, a reliable interpretation and (to a certain extent) the prediction of the properties of the materials that are to be used in heterogeneous catalysis and expected to act as a reforming catalyst.

In our present study we concentrated on the adsorption of both chain and aromatic hydrocarbons in the support and catalyst model. To explicitly assess the effect of the active metal (spread onto the support) on the said physicochemical phenomena, we decided to neglect the formation of carbon deposits on the catalyst surface, which contributes to the poisoning of the active sites produced by platinum. Analysis was carried out with the Cerius² software (Accelrys), which, owing to its graphic interface, enabled a perfect visualization of the phenomena under study.

3. Methods

The Cerius² software is a set of tools (based on molecular mechanics methods) supporting the investigations of the adsorption phenomenon in microporous materials.

The possibilities offered by the software were adopted to the examinations of the host (support, reforming catalyst)–

guest (heptane, methylcyclohexane, toluene) system. The interactions between the atoms of the support/reforming catalyst structure and the molecules of the hydrocarbons were calculated by the forcefields method, which is used in molecular mechanics. The method involves a set of functions (derived from the principles of classical mechanics) and terms required for their parametrization (force constants, equilibrium bond lengths and angles, etc.) in order to describe the state of energy for the entire group of molecules with sufficient accuracy. This can be achieved by interpolating or extrapolating the empirical data for a small group of molecules onto a larger group of similar structures [6]. There are forcefields which describe the behavior of a small atom group with a high accuracy, but when a larger group of atoms is to be described, accuracy will suffer from limitation. The use of empirical data to describe the state of the entire group of molecules is of great advantage in that this reduces remarkably the demand for computational capacity compared to the use of *ab initio* [7,8]. Owing to this advantage, simulations of much larger models have become feasible. When use is made of the *ab initio* methods to simulate models of a size as large as several thousand atoms, such simulations will be far beyond the capacity of a today's computer mainly because of the demand for appropriate computational time and memory usage. The application of the forcefield method eliminates those drawbacks. Our computations were carried out with the UFF method recommended by the software producer. The UFF had been tested with similar systems containing all the atoms of which the models used in the present study were built [7–9]. The comparison of calculated and experimental results raises problems because of the properties of the model that was used for the needs of our study. Al₂O₃ has a specific, irregular porous structure; in real models, pore size varies between several and several thousand

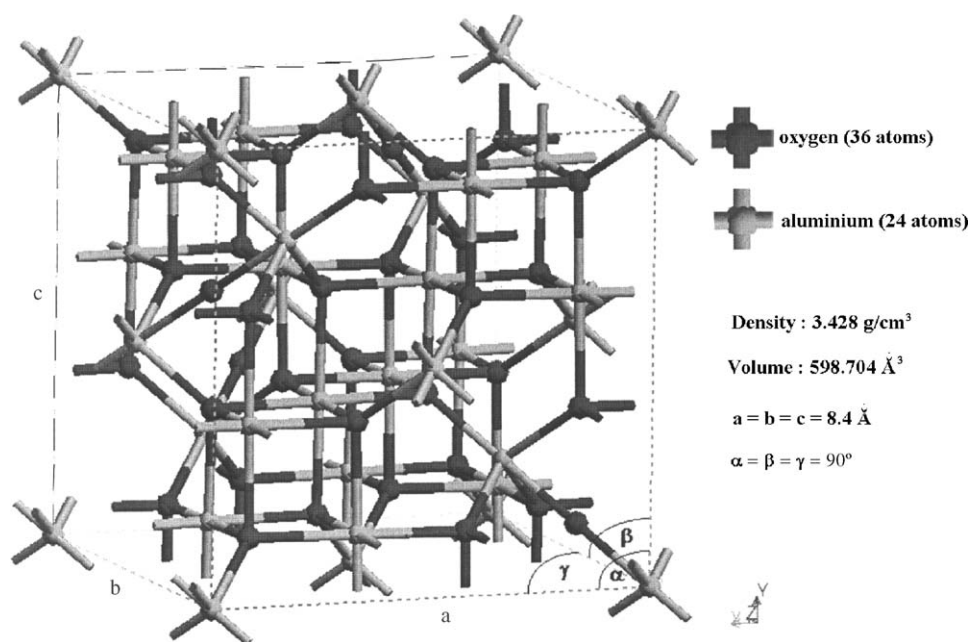


Fig. 1. The elementary cell of γ -Al₂O₃ support.

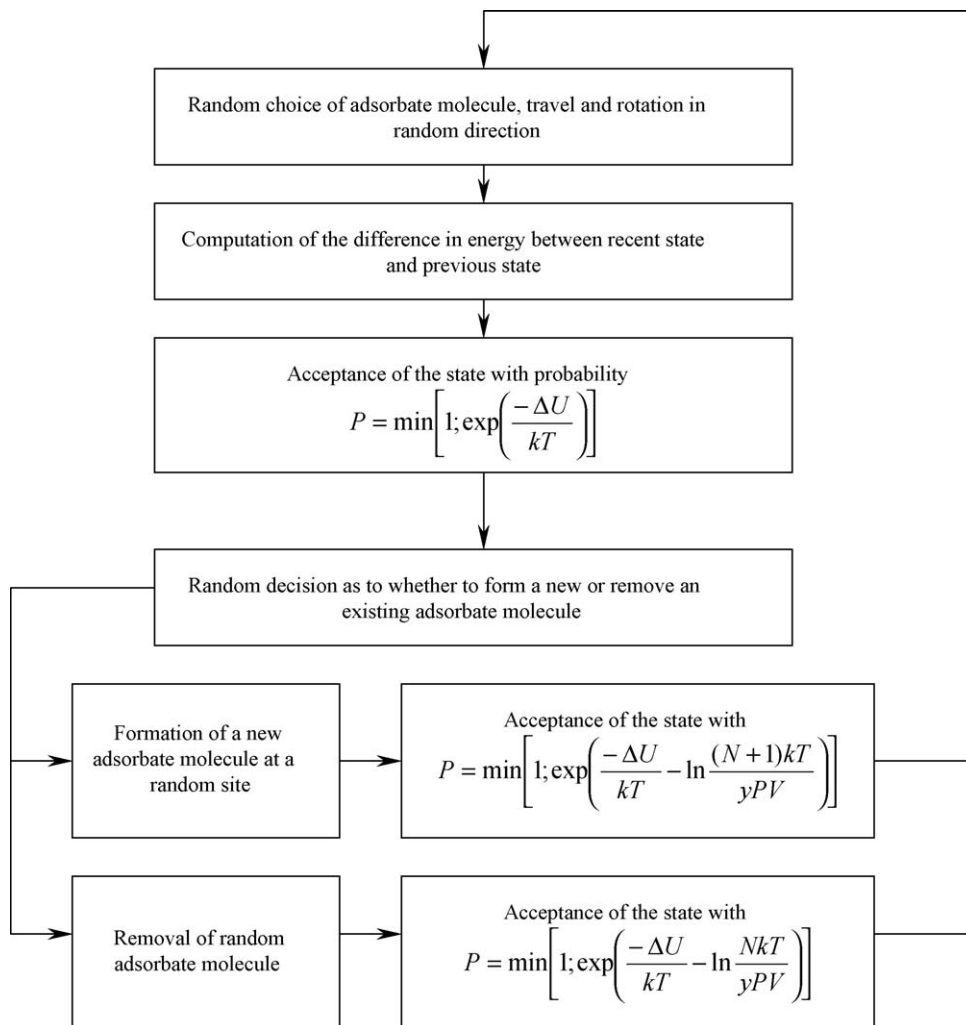
angstroms. The near-surface behaviour of small organic molecules depends much on the micropore size. We adopted quite a simplified model that should be treated as depicting a small fragment of a real system. Any comparison of the data obtained using such a model with the results obtained by experiments will promote errors. For these reasons, our study did not aim at verifying the reliability of the model adopted for calculations; it concentrated on the analysis of the physicochemical phenomena that occur in a particular fragment (one out of the potential fragments, though difficult to reproduce) of the real system.

3.1. Preparation of models

The elementary cell γ -Al₂O₃ [10] for the models of the adsorbents used in this study was read in from the library of the Cerius² software (Fig. 1) and had the following parameters—periodicity: 3-D, atoms: 60, volume: 592.704 Å³, density: 3.428 g/cm³, cell formula: O-36; Al-24, $a = b = c = 8.4$ Å, $\alpha = \beta = \gamma = 90^\circ$.

To prepare the adsorbent model for the purpose of simulation by using an elementary cell which comes from the software library, we carried out the following operations:

1. The elementary cell γ -Al₂O₃ was multiplied along the x -, y - and z -axes until the model attained the size of several elementary cells (approximately 2000 atoms); then a supercell was formed, where each atom was independent and its coordinates did not result from the symmetry operation.
2. In the supercell, pores of different size were formed by the removal of atoms to make the model resemble the structure of a real catalyst support. With the help of a special subroutine we obtained pores whose radii varied along their lengths, thus accounting for their bottle neck shape.
3. To build the catalyst model (Pt/ γ -Al₂O₃), we donated the support model (γ -Al₂O₃) which had been prepared earlier, with platinum by replacing Al atoms with Pt atoms in such a way that the ratio of Pt atoms to the other atoms (oxygen and aluminium) approached 4 wt.%. This value is not consistent with the values for catalysts of industrial use. However, if we wanted to keep the proportion required, this would necessitate the construction of a much larger support/catalyst model and in consequence remarkably extend the computational time.
4. The formation of the pore, as well as the donation of the support with platinum, disturbed the ideal crystalline



Scheme 1. Simulation of sorption by the Monte Carlo method.

structure, which necessitated minimizing the energy of the system. To achieve this, we used the open forcefield (off.exe), a part of the Cerius² software. Thus, the structure was regarded as being optimal when the value of the mean square root of the derivative fell below 0.001 kcal/mol/Å. This condition was fulfilled after approximately 500 simulation steps on average.

3.2. Adsorption equilibrium

It is conventional to describe the adsorption equilibrium by adsorption isotherms, which relate the amount of the substance adsorbed to pressure, at a constant temperature, $N = f(p)_T$. The adsorption isotherm clearly describes the adsorbing capacity of the investigated adsorbent–adsorbate system and enables the adsorbent to be assessed in terms of its catalytic properties. At low gas pressure, the amount of molecules adsorbed per unit surface is in direct proportion to the pressure in the volumetric phase, so it can be described by the simplest equation of the adsorption isotherm:

$$N = K_H p \quad (1)$$

where K_H is Henry constant, N denotes the amount of molecules adsorbed, and p stands for pressure.

Molecular simulation techniques such as that of Monte Carlo (MC) offer effective modes of assessing the parameters that describe adsorption. They all have been verified in researches on the adsorption of a diversity of molecules [11–13] in a variety of pore structures, slitlike, cylindrical, spherical and a zeolitic [14–16]. Simulations of the state of phase equilibrium require that the computational algorithm should include the potentials of the chemical molecules. The computational method proposed by Cerius² for the adsorption isotherm is based on the principle that new molecules are added and existing ones are removed. What follows is the mass exchange between the system observed and the immediate environment, the corresponding statistical system being the grand-canonical PVT ensemble, where the number of molecules changes so as to maintain constant values of pressure, volume and temperature. The conditions specified above are fulfilled when use is made of Monte-Carlo simulations in the grand-canonical ensemble (GCMC). Particular steps of the simulation procedure are shown in Scheme 1.

The foregoing algorithm can be divided into two steps. One is responsible for the travel of the adsorbate molecules inside the pore, the other one for the formation and removal of the molecules. Normally, the initial configuration of the system does not include adsorbate molecules, so step one is negligible for obvious reasons until a new molecule is formed in step two. While the new molecule is forming inside the pore, its position is randomly selected. Thereafter the energy of the new state is calculated. In the case of removal, a randomly selected molecule is drawn away from the system, and then the new energy is computed. The new configuration is accepted with a certain probability. If the attempt to remove the adsorbate molecule fails, the molecule will retain its initial position. The Henry constant which is defined as the slope of the adsorption

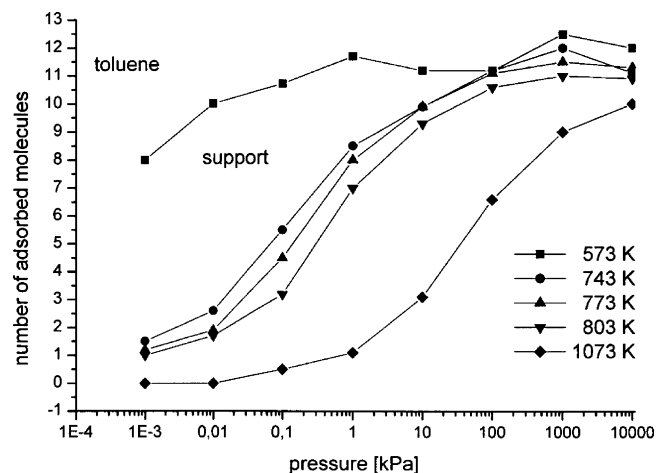


Fig. 2. Adsorption isotherms for toluene in the γ -Al₂O₃ structure (support) at different temperature.

isotherm when pressure tends to zero, can be computed directly from the configuration integral of the system [17]:

$$K_H = \frac{1}{kT} \int_V \exp \left[\frac{-U}{kT} \right] dr \quad (2)$$

Integration is carried out over the entire volume of the system. The procedure has to be repeated a statistically significant number of times.

4. Results and discussion

4.1. Support model, reforming catalyst model, simulation conditions

Both the support and reforming catalyst models were prepared by the methods described in Section 3.1 and thereafter used for simulating the sorption of the reagents involved in the reforming process. After minimizing the energy of the system, simulations of the sorption phenomenon were carried out with the two models (sorbents), using the MC method described in

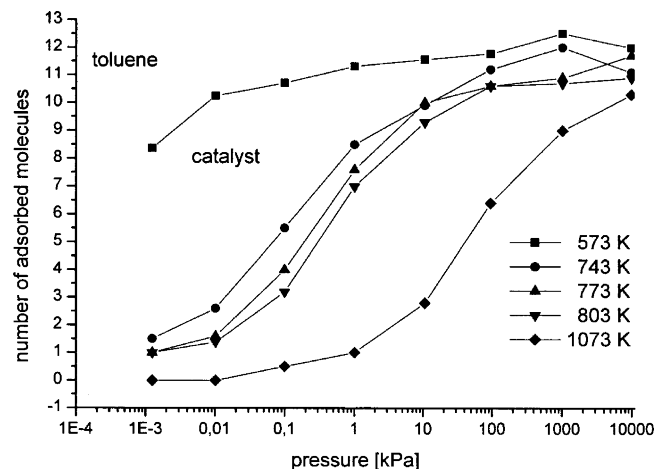


Fig. 3. Adsorption isotherms for toluene in the Pt/ γ -Al₂O₃ structure (catalyst) at different temperature.

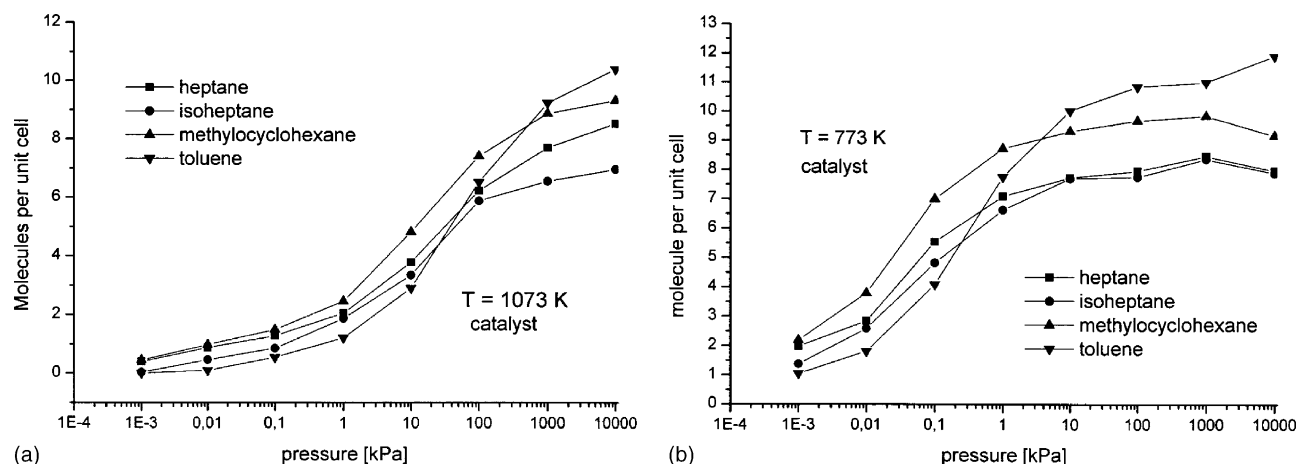


Fig. 4. Adsorption isotherms for heptane, 3-ethylpentane, methylocyclohexane and toluene in the Pt/ γ -Al₂O₃ structure (catalyst) at (a) 1073 K; (b) 773 K.

Section 3.2. Heptane, isoheptane, methylocyclohexane and toluene models acted as sorbates, their molecules being build as proposed in the Cerius² software.

Simulations were performed at 573, 743, 773, 803 and 1073 K in the grand-canonical statistical ensemble. Computations were conducted with Forcefield Universal [18–20]. Equilibrium of the system was achieved after approximately 3 million iterations (Scheme 1).

4.2. Adsorption isotherms

According to expectations, the number of the molecules adsorbed in the supercell rose with increasing pressure (Figs. 2 and 3). The rise in temperature inhibited adsorption, which manifested in the reduced amount of molecules adsorbed. The lowest of the investigated temperatures notably facilitated adsorption. As shown by the plots in Figs. 2 and 3, a pressure of

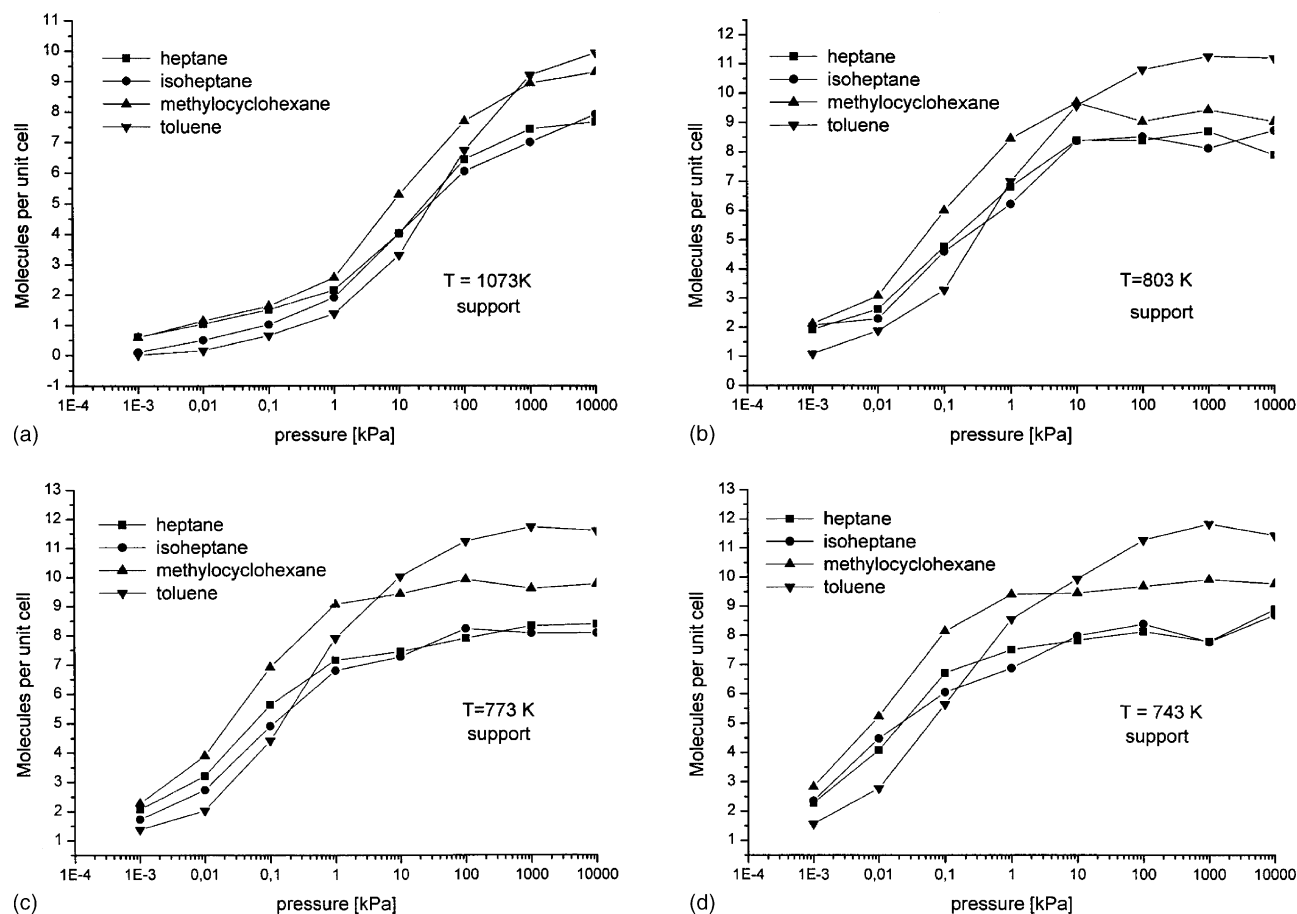


Fig. 5. Adsorption isotherms for heptane, 3-ethylpentane, methylocyclohexane and toluene in the γ -Al₂O₃ structure (support) at (a) 1073 K; (b) 803 K; (c) 773 K; (d) 743 K.

about 10^{-1} kPa was sufficient to provide saturation of all the active sites by toluene in both models when temperature amounted to 573 K. As temperature rises, adsorption becomes inhibited, and saturation of the active centers by toluene will be attained only at noticeably higher pressure. Thus, at 1073 K, even the highest of the investigated pressures, 10^4 kPa, did not suffice to make toluene saturate all of the adsorption centers. The Henry constant for toluene is low, which indicates that, at low pressure, toluene adsorbs at a poorer rate than do the other investigated sorbates (Figs. 6 and 7) but when pressure takes a high value (10^4 kPa), the amount of toluene is greater than that of the other sorbates. This finding holds for the catalyst (Pt/ γ - Al_2O_3) (Fig. 4(a and b)) and support (γ - Al_2O_3) models at all investigated temperatures (Fig. 5(a–d)). The maximal number of toluene molecules adsorbed per elementary cell amounted to 12, while that of heptane molecules was only 8 under the same conditions. This should be attributed to the volume of the toluene molecule, which is smaller compared to the molecules of the other investigated sorbates.

A comparison of the adsorption isotherms for various hydrocarbons in the same support/catalyst model (Figs. 4a and b and 5a–d) shows conclusively that at low pressure adsorption of toluene is very difficult, irrespective of the model and simulation temperature applied. The number of molecules adsorbed per elementary cell is also the lowest with this hydrocarbon. Under the same conditions, the adsorption of the other hydrocarbons (heptane, isoheptane and methylcyclohexane)

is visibly easier. The opposite holds for the application of high pressure. Toluene adsorbs very easily, and the number of toluene molecules adsorbed per elementary cell is the highest compared with heptane, isoheptane and methylcyclohexane. Thus, with the support model at 1073 K (Fig. 5(a)), there is a distinct rise in the number of molecules at the pressure of 10 kPa. From approximately 50 kPa on, the number of toluene molecules is greater than that of heptane molecules, and with 500 kPa and higher pressure values greater than that of methylcyclohexane molecules. Platinum exerts no significant effect on the amount of the hydrocarbons adsorbed, so the plots of the adsorption isotherms do not change (Fig. 4(a)). It should be noted that for both the models the number of heptane molecules is always smaller than the number of methylcyclohexane molecules adsorbed over the whole range of the pressure applied. At temperature lower than 1073 K, there is visible adsorption of all hydrocarbons in the initial range of pressure. The adsorption isotherm for toluene intersects that for heptane at about 0.5 kPa and that for methylcyclohexane at about 5 kPa (Figs. 4b and 5b). Hence, the points of intersection shift towards low pressure values with decreasing temperature (Figs. 4a and b and 5a–d). It is recommended (in terms of adsorption) that the main reaction of the reforming process (dehydrocyclization) should be conducted at a pressure allowing the lowest adsorption of toluene and the highest adsorption of heptane. The point is that the reaction product (toluene) should not block the active centers of the catalyst which have been

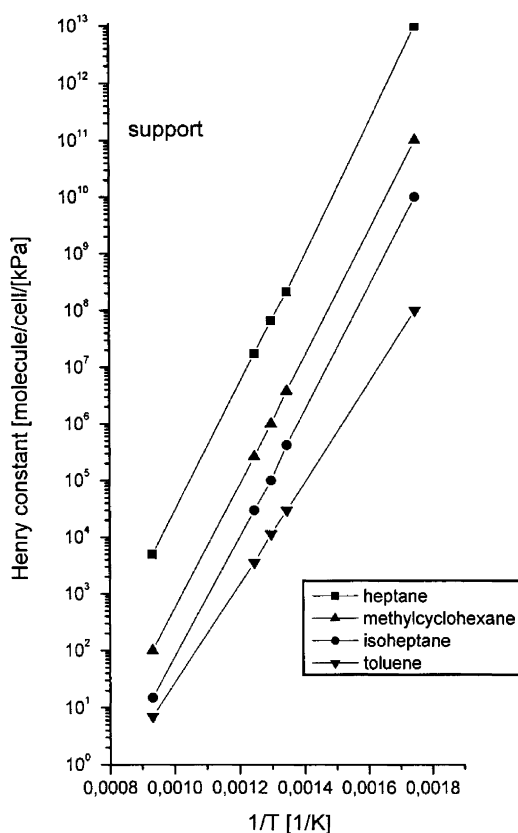


Fig. 6. Temperature dependence of Henry constant for adsorption of heptane, 3-ethylpentane, methylcyclohexane, and toluene; host: γ - Al_2O_3 —support.

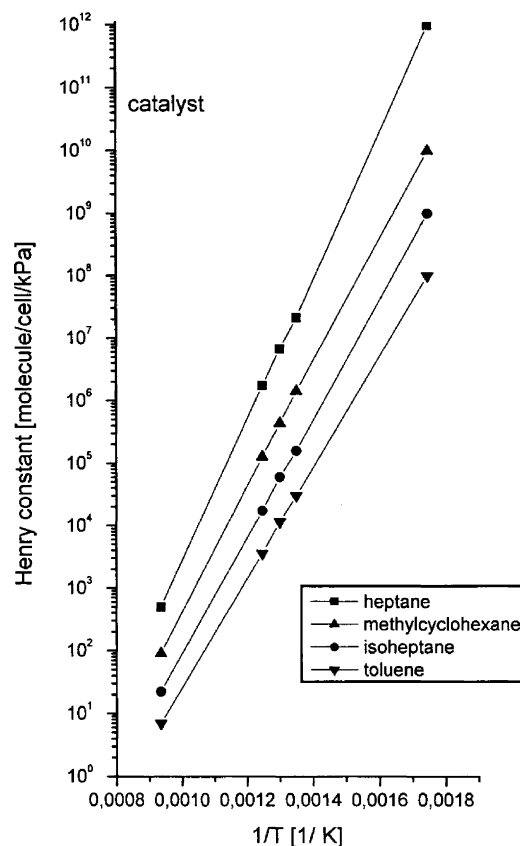


Fig. 7. Temperature dependence of Henry constant for adsorption of heptane, 3-ethylpentane, methylcyclohexane, and toluene; host: Pt/ γ - Al_2O_3 —catalyst.

designed for the raw feed material (heptane). As demonstrated, at high pressure it is toluene that saturates the active sites, thus slowing down the desired dehydrocyclization reaction. On the other hand, if we decrease the process pressure, this may soon produce coke-poisoning of the catalyst. If we raise the process temperature, this will shift the point of intersection for the isotherms of toluene adsorption and heptane adsorption towards higher pressures, thus allowing the adsorption of *n*-heptane to prevail over that of toluene within a wider pressure range; in some instances, however, this may account for the excess cracking of the raw material. These findings substantiate the need for research on the improvement of reforming catalysts so that the process would be conducted at decreased pressure and increased temperature. At present, bimetallic catalysts (Pt-Re/ γ -Al₂O₃) respond partly to such requirements.

The temperature dependence of the Henry constant (Figs. 6 and 7) confirms the conclusions drawn from the analysis of the adsorption isotherms. As shown by these plots, the constant (for

both models and all investigated temperatures) takes the lowest and the highest value with toluene and heptane, respectively. This is an indication that the amount of the toluene molecules adsorbed increases at a slower rate when pressure is low. It should, furthermore, be noted that temperatures of the lower investigated range increase the difference in the Henry constant between heptane and toluene, which implies that in the lower range of the investigated temperatures (in the lower range of the investigated pressure) the difference in adsorption between the two hydrocarbons increases.

4.3. Mass distribution

Figs. 8–10 show the mass distributions for the molecules of the sorbates adsorbed in the support and catalyst structures at 773 K and 10⁴ kPa. Each point in the figure indicates the center of the hydrocarbon molecule mass. The color of the point describes the energy of the molecule at the given adsorption site

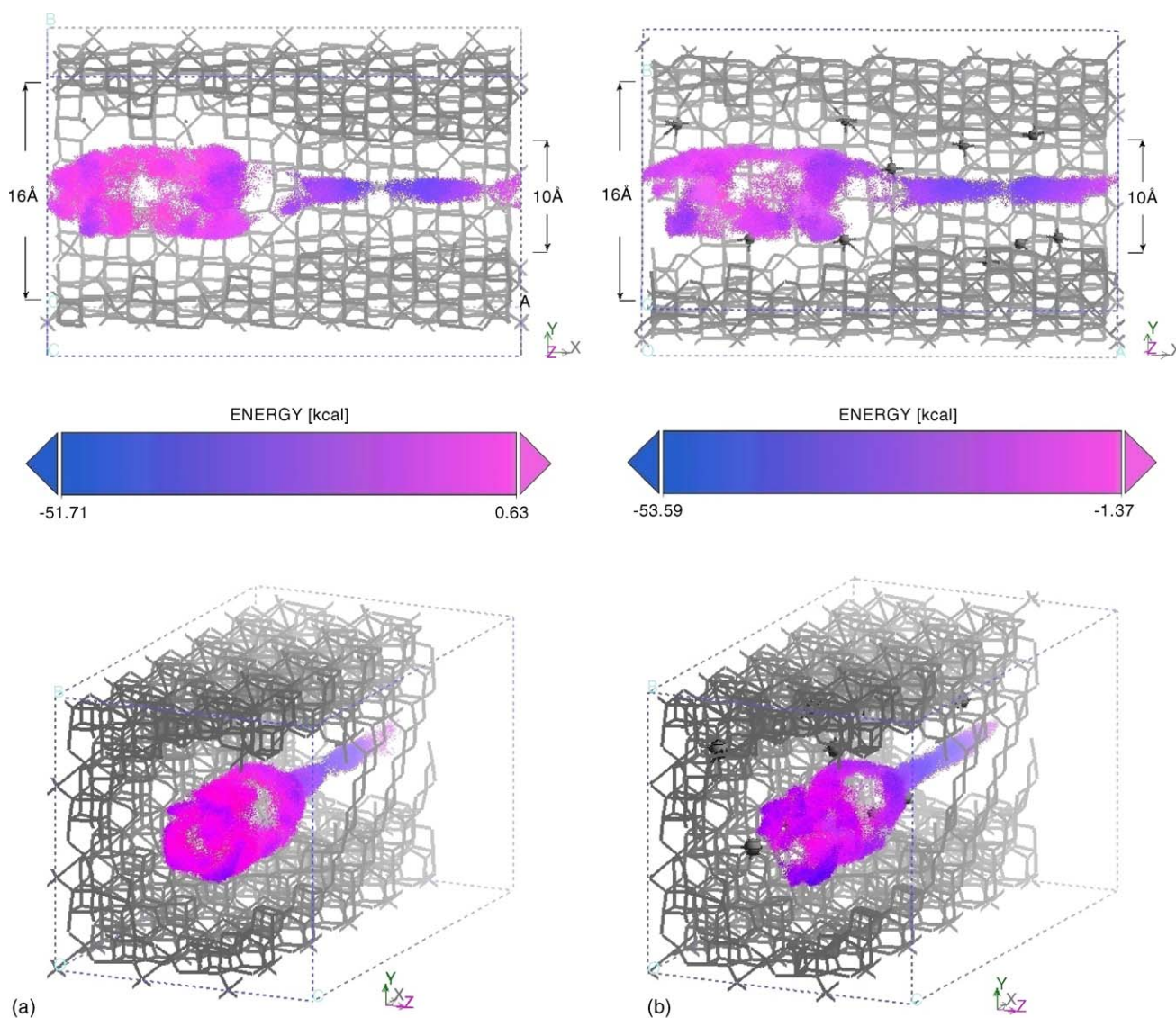


Fig. 8. Mass distribution of heptane in the γ -Al₂O₃ structure at 1073 K and 10⁴ kPa; (a) bottle neck model—support; (b) bottle neck model donated with platinum—catalyst.

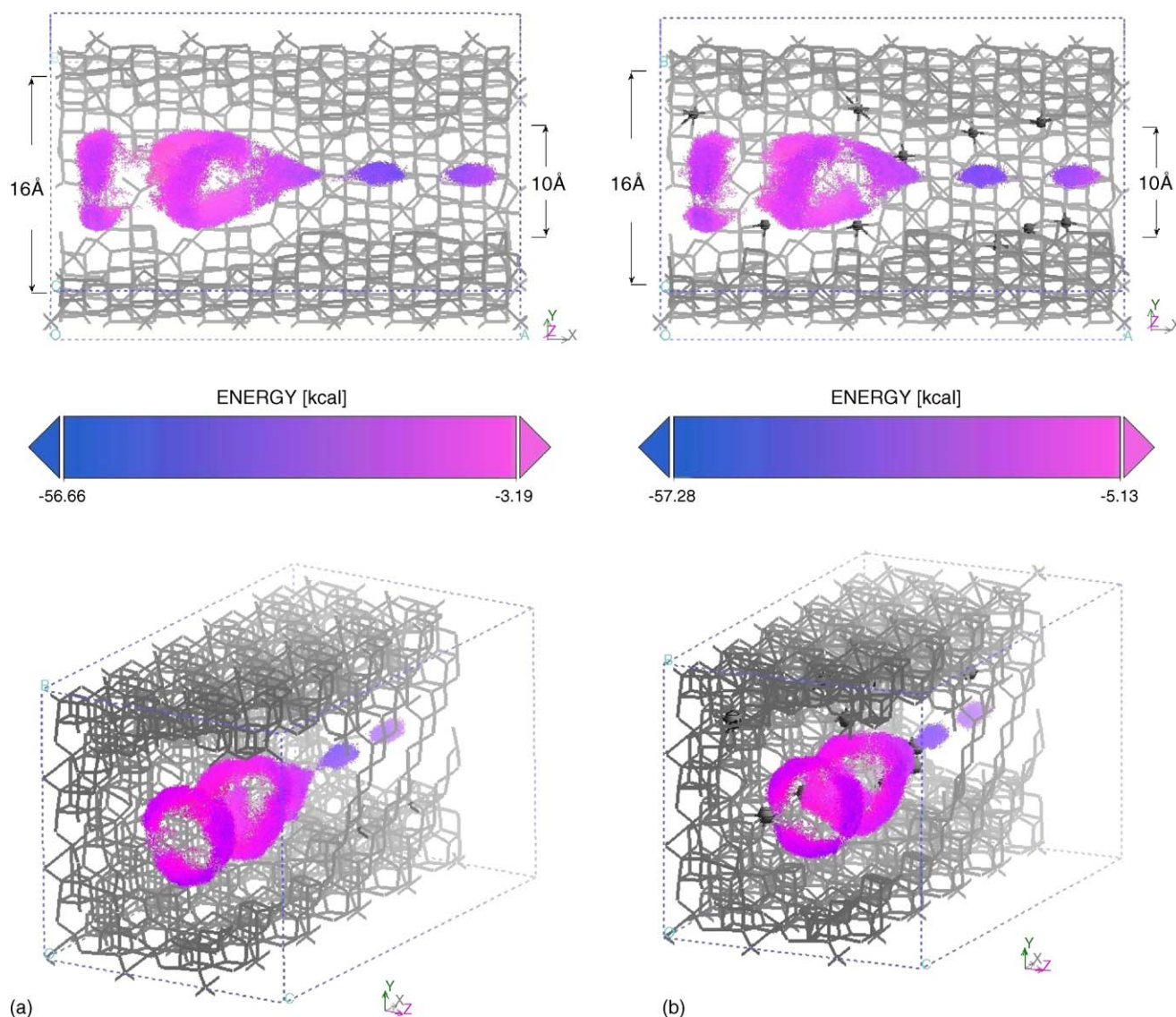


Fig. 9. Mass distribution of methycyclohexane in the γ - Al_2O_3 structure at 1073 K and 10^4 kPa, (a) bottle neck model—support; (b) bottle neck model donated with platinum—catalyst.

(blue and red points refer to low and high energy, respectively). Each figure includes a color scale which takes similar values for each of the hydrocarbons studied. The minimal energy values range from -61.13 kcal for the adsorption of methycyclohexane in the model with no platinum to -48.76 kcal for the adsorption of toluene in the Pt-donated model, the maximal energy values varying from -0.33 kcal for toluene adsorption in the model without platinum to 2.28 kcal for toluene adsorption in the Pt-enriched model. As shown by the plots in Figs. 8–10, both small and large diameter pores are accessible to the sorbates. Yet, they prefer sites only at certain points of the structure; they do not locate over the entire volume but just form characteristic rings in the wide part of the pore. In the narrow part two characteristic clusters are formed. In the narrowing between the pore of 16 Å diameter and that of 10 Å diameter heptane and cyclic hydrocarbons follow a different behavioral pattern. Toluene and methycyclohexane show a

greater ease than heptane does to locate at that site, where they form a characteristic ‘cone’. Heptane does not adsorb in the narrowing of the micropore, but this cannot be attributed to the shape of the molecule. The heptane molecule is long, narrow, flexible and capable of producing conformers, which is an indication that steric hindrance cannot be regarded as the contributing factor. The likely cause is interaction energy. It should be noted that the negative interaction energy values under study substantiate an easy adsorption on the walls of the micropores, which intensifies with decreasing interaction energy. As the interaction energies of the investigated hydrocarbons take similar values, this is an indication that, despite the differences between them, the hydrocarbons follow similar patterns of adsorption.

A characteristic feature is the considerable decrease of adsorption energy in both models for all of the hydrocarbons in

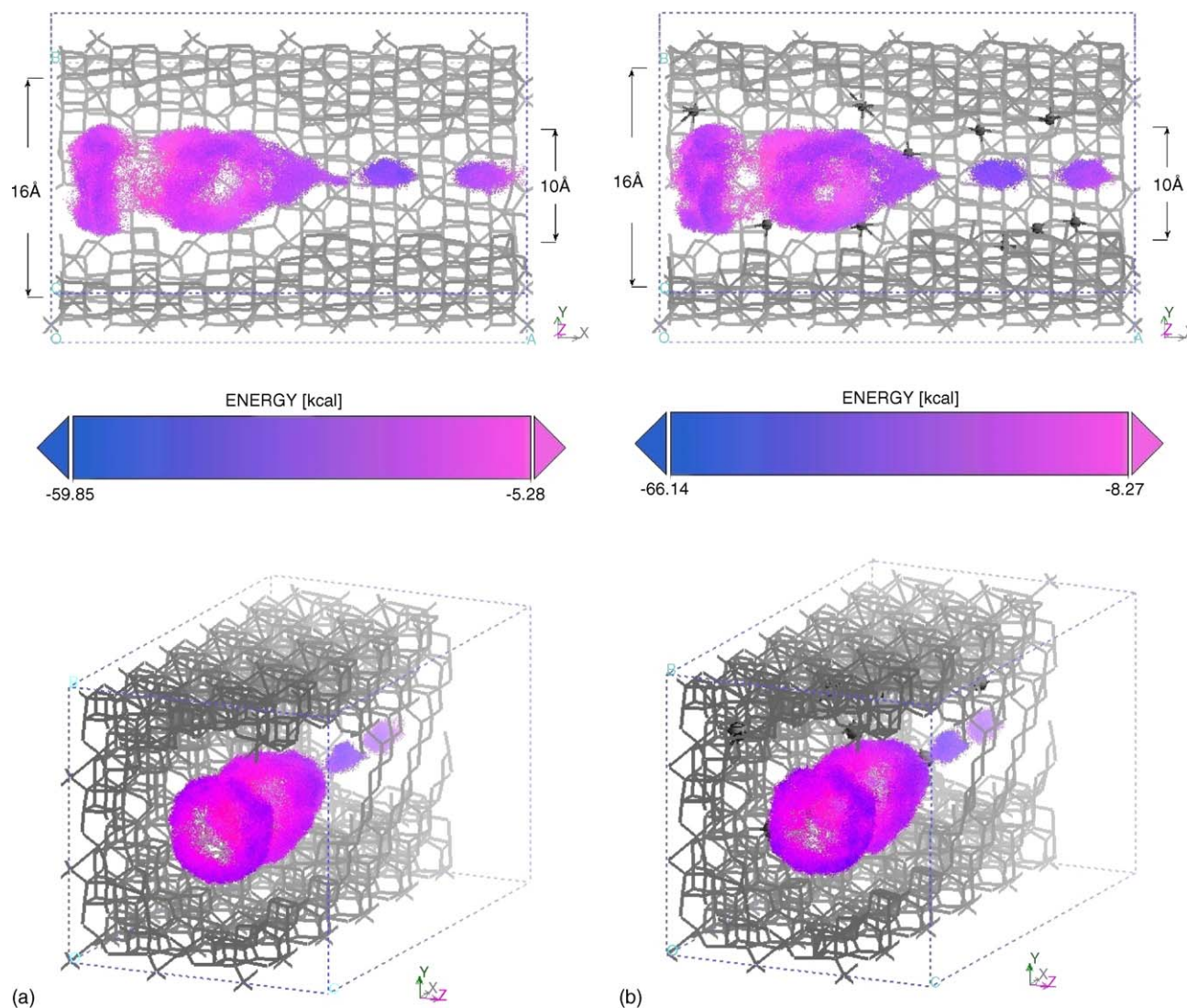


Fig. 10. Mass distribution of toluene in the γ - Al_2O_3 structure at 1073 K and 10^4 kPa, (a) bottle neck model—support; (b) bottle neck model donated with platinum—catalyst.

the micropore fragment of a small diameter. The majority of the molecules adsorbed there display energies lower by even several dozen kilocalories compared to those adsorbed in the wide part of the micropore. This remarkable drop in energy is probably due to the proximity of the micropore walls. The negative host–guest energy facilitates adsorption, and the proximity of the support/catalyst atoms in the narrow micropore gives rise to advantageous interactions on each side of the adsorbed molecule.

The considerable decrease in energy – and consequently the intensified adsorption in the narrow micropores – promotes the immobilization of the molecules in the narrow micropore, as well as the formation of visible clusters. This does not hold for heptane molecules, when the mass cloud in the narrow micropore of the catalyst is blurred. Since the energy values are similar in every instance, the cause may lie in the oblong shape of the heptane molecule, which has a greater ease to move between the adsorption centers at

elevated temperature. In this context it is possible to assume that surface diffusion may occur. Such mechanism can be regarded as responsible for the formation of those characteristic rings in the wide part of the micropore, where the molecules adsorb close to the walls while the central part remains unsaturated.

Figs. 8–10 display a decrease in the interaction energy of the hydrocarbons in the Pt-donated model. What substantiates this finding is a greater number of blue than red points in the mass cloud. The same holds for each of the investigated hydrocarbons at any of the temperatures applied and may indicate that adsorption in the proximity of the platinum centers is easier.

5. Conclusions

Analyses of the adsorption isotherms, Henry constants and mass clouds of the hydrocarbon molecules adsorbed in the

catalyst structure have confirmed that the efficiency of reforming can be upgraded by reducing the pressure and raising the temperature of the process. The characteristic shape of the adsorption isotherm for toluene, differing from the shapes of the other adsorption isotherms, allows the conclusion that by controlling the ratio of heptane adsorption to toluene adsorption via temperature and pressure changes may favourably influence the efficiency of the process. The shapes of the adsorption isotherms and the values of the Henry constants show that at low pressure the adsorption of toluene is far more difficult than that of the other hydrocarbons; at high pressure, toluene adsorbs easier than does heptane or methylcyclohexane, thus blocking the active centers of the catalyst. A rise in temperature inhibits the adsorption of all the hydrocarbons studied, and the active sites become saturated at noticeably higher pressure.

Adsorbing hydrocarbons prefer only certain points of the structure; in larger pores, they form characteristic rings, in narrow pores and in pore narrowings they build clusters and (ring-like) ‘cones’, respectively. At 1073 K, the ‘trapped clusters’ of the adsorbed heptane (in narrow pores) tend to blur, which can be attributed to a poorer adsorption and an increase in diffusivity.

Summing up:

- As pressure increases, so does the number of molecules adsorbed in the supercell. This finding conforms to the Henry constant values. The lowest values are with toluene, which corresponds with the lowest slope of the adsorption isotherm at pressure tending to zero.
- A rise in temperature inhibits adsorption. Adsorption sites become saturated at remarkably higher pressure.
- At low pressure, toluene adsorbs slowly in the support model; the number of molecules adsorbed there is the lowest of all the hydrocarbons studied. The opposite is true for high pressure, as under such conditions adsorption is facilitated and the number of toluene molecules adsorbed is the highest compared to the other hydrocarbons.
- In the pore fragment of a small diameter, a decrease in adsorption energy is observed in each of the catalyst models and with all the hydrocarbons. Compared to the molecules adsorbed in the large diameter part of the micropore, the majority of those adsorbed in the small diameter fragment display energies lower by even several dozen kilocalories.
- The greater number of blue points in the mass cloud suggests a decrease in the interaction energy of the hydrocarbons in the Pt-donated model.

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