

Simulating adsorption of *n*-heptane in the Pt/Al₂O₃ model: Influence of platinum

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Abstract

The molecular modeling method referred to in the literature as Grand Canonical Monte Carlo was used to analyze the phenomenon of *n*-heptane adsorption on the Pt/γ-Al₂O₃ catalyst. In order to describe relevant interactions, use was made of the forcefield methods (UFF and CVFF). With the conditions adopted for the purpose of the study, Pt was found to exert an advantageous effect on the adsorption of *n*-heptane. The number of adsorbed molecules was related to the content of the noble metal, and the relation was directly proportional, when temperature and pressure were constant. The contribution of Pt was most distinct at 573 K and 100 kPa.

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1. Introduction

Every reaction over a heterogeneous catalyst should be regarded as a multi-stage process, which involves diffusion of the substrates through micropores, adsorption on the catalyst surface, a chemical reaction, as well as the desorption and diffusion of the products. Each of these stages contributes to the overall efficiency of the catalyst.

In our study, information on the course of adsorption was difficult to obtain by experiments because the conditions applied favor the occurrence of the reaction. For this reason, use was made of computer simulations as a convenient alternative [1].

The process of crude oil reforming – but primarily the principal reaction, i.e., the dehydrocyclization of paraffins – is a catalytic one [2]. The reaction products are aromatic hydrocarbons, and the catalyst used for the needs of this process is a bifunctional, Pt-based catalyst [3]. The reaction itself proceeds either via a monofunctional [4] or bifunctional mechanism. The latter has been reported as controlled by the acid function [5] or metal function [6]. With a fresh catalyst,

dehydrocyclization on the metal function is important, but after several hours on the stream the acid function becomes the controlling function for this mechanism [7].

In this study, the molecular modeling methods were used to determine the effect of platinum on the adsorption of *n*-heptane over Pt/γ-Al₂O₃ catalyst. The sorption phenomenon was analyzed, considering that the model reaction of reforming (dehydrocyclization of *n*-heptane) will run on the above catalyst.

2. Model and computational details

The construction of the right model is a key issue in every computer simulation. On the one hand, the model is supposed to reflect a real system as closely as possible to make sure that the results are adequate. On the other hand, model simplifications are amongst the advantages, which a computer simulation can offer. In this way, it is possible to eliminate the undesired factors that might affect the results obtained. What is more, a simplified model structure needs far less computation time.

The model used in the present study was designed so as to achieve sufficiently accurate results with a comparatively

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simple structure and the lowest possible computational costs involved. To describe the energy of the system use was made of the forcefield method, which yields sufficiently accurate results and involves comparatively low computational costs.

The UFF was used to optimize the geometry of all the models, those containing Pt (catalyst) and those with no Pt content (support). The comparison of the optimized model geometry with the crystallographic data made use of when constructing our models substantiated the choice of the UFF. Unfortunately, “reference points” like adsorption isotherms that might be of utility in examining the reliability of the forcefield approach to sorption are lacking. Under conditions adopted for the simulations, the Pt/Al₂O₃–heptane system, which is a highly reactive one, would have very soon reached a state of equilibrium with respect to many hydrocarbons. Our choice of the CVFF was supported by the observation that heptane adsorption resulting from the simulation in the UFF was too intense even at low pressure.

Specialized literature includes many references to forcefields whose parameters have been optimized for particular groups of chemical compounds. In agreement to our previous study [8], the forcefield used was the CVFF, with the following Pt parameters: $A_i = 4,576,819.9618$ and $B_i = 16,963.30818$. These parameters have been included in the CVFF added to Cerius². They are not part of the original CVFF developed by Hagler et al. [9–16]; they have been introduced into the forcefield by the Accelrys group, making use of the paper by Halicioglu et al. [17]. We did not modify the forcefields for the need of our study either in the range of atom parameters or in the functional form.

Reforming catalysts are supported on gamma aluminum oxide. We are aware of controversies surrounding the γ -Al₂O₃ structure. Upon examination of different literature sources, we found three structures described as γ -Al₂O₃ which differed completely from one another. The inconsistencies that occur in such cases are practically unavoidable. That is why we decided to make use of the structure derived from the Cerius² data base [18] without any modifications.

Since a single elementary cell was not large enough to include the micropore, it seemed advisable to use a set of 112 elementary cells forming $24 \times 24 \times 56$ Å cuboid ($4 \times 4 \times 7$) cells as the basic unit. In the supercell obtained in this way, a cylindrical micropore of a 20 Å diameter was formed and located in parallel to the longer walls. The micropore was set up in the $\langle 100 \rangle$ direction, which is identical to the $\langle 010 \rangle$ and $\langle 001 \rangle$ because of symmetry. There were 40, 46 and 14% of Al atoms of coordination 4, 5 and 6 respectively, as well as 2.7% of dangling bonds, on the pore surface.

The shape and the size of the micropore were chosen arbitrarily. The porous structure of the γ -Al₂O₃ catalyst is highly irregular, with a pore size varying from several Å (micropores developing the catalyst surface) to several thousand Å (macropores responsible for the transport of

reagents). Adsorption of reforming reagents occurs in micropores of diameters ranging between several and several dozen Å, so we decided to use this pore size in our models.

We are aware of the fact that the γ -Al₂O₃ surface is hydroxylated and the charge of the –OH group is much lower. However, considering the interactions with hydrocarbons, which are non-polar molecules, this seems to be of lesser importance.

On the basis of this support model, 9 catalyst models differing in platinum content (from 1 to 9 atoms per supercell, which is an equivalent of 0.20–1.84 wt.%) were constructed. Platinum (in oxidation state +4) was incorporated into the micropore surface via oxygen bridges [19,20]. The model containing nine Pt atoms is shown in Fig. 1a. With the cluster (particle) of Pt the situation is different. It certainly has the form of a metal-like particle; but – similarly to what has been assumed in the case of single Pt atoms – it is connected to the support by way of three oxygen bridges. For that reason it is difficult to clearly define the oxidation state

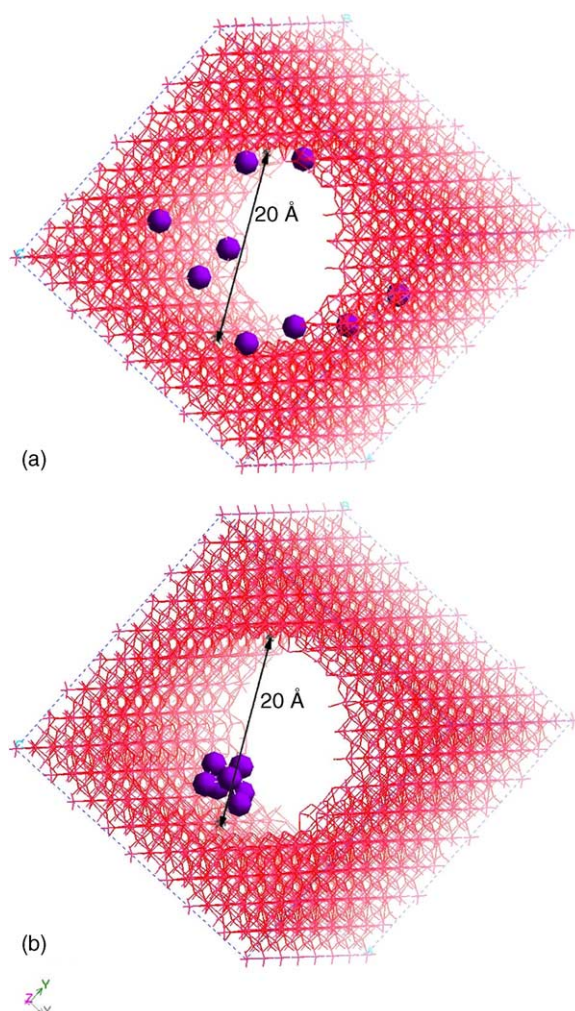


Fig. 1. Computational models.

for particular Pt atoms in such a structure. The model containing a Pt particle which consisted of seven Pt atoms (1.43 wt.% of Pt) is shown on Fig. 1b.

The modification of the system (by the formation of the micropore and substitution of Al atoms with Pt atoms) brought about a disorder of the crystalline structure, thus raising the need of optimizing the geometry of the model. Minimization was carried out using the universal forcefield (UFF) [21–23] and conjugate gradient [24] method.

The grand canonical monte carlo (GCMC) approach (made use of in a previous study of ours for the analysis of *n*-heptane adsorption over the Pt/Al₂O₃ catalyst) is a stochastic method, where the randomly selected host–guest positions are either accepted or rejected, depending on the energetic criterion. A new state of the system can be generated via different methods: by translation or rotation of a selected guest molecule, which is present in the system; by the formation of an additional guest molecule or removal of the adsorbed one. After each change in the state of the system, its energy is calculated, and this is the factor that affects the probability of whether the changed state will be accepted or rejected. The procedure is repeated in order to achieve an equilibrium between the number of accepted states and that of rejected states, as such equilibrium is equivalent to the achievement of thermodynamic equilibrium. The number of the steps required to achieve equilibrium differed according to the pressure acting in the system and varied from 1 to 12.5 million. The pressure range for the needs of the study was chosen in the following way: at the lowest pressure adopted for calculations, *n*-heptane adsorbed only slightly inside the micropore. Then the pressure was increased 10-fold until the guest occupied all the available sites, and a further rise in pressure yielded no increase in the number of adsorbed molecules.

Considering the flexibility of the heptane molecule, it was necessary to take into account the conformations of the molecule that might occur in the system at elevated temperature. To find the potential conformations, molecular dynamics simulations were carried out for an isolated *n*-heptane molecule at 1073 K. They yielded a set of 10 possible conformations, which were used in subsequent adsorption simulations.

We did not apply molecular relaxation at each MC step. If we did, the time needed to perform the simulation would be far too long, taking into account the assumptions formulated for the purpose of the study (number of catalyst models; investigated pressure and temperature ranges).

The GCMC procedure requires the imposition of some periodic conditions on the system to be simulated. Thus, it is assumed that the system must be treated as an infinite one, built of identical periodic boxes adjacent to each other. It is convenient to regard the supercell as an elementary box.

Simulations were carried out at a temperature ranging between 573 and 1073 K for each model under test. For comparison, simulation was also performed with a model where platinum was absent.

3. Results and discussion

With the method described here we were able to compute the equilibrium number of the *n*-heptane molecules adsorbed in each of the investigated systems. Relevant adsorption isotherms at 773 K are plotted in Fig. 2.

As shown by these plots, the number of adsorbed *n*-heptane molecules rises with increasing pressure. This was expected to happen because elevated pressure makes the equilibrium shift towards adsorption. The reverse is true for the effect of temperature on adsorption: the number of the molecules adsorbed decreases with increasing temperature. Such behavioral pattern has been expected because the rise in temperature is supposed to promote the desorption of the molecules from the host surface.

Analogous plots of the adsorption isotherm have been obtained with all Pt-containing catalyst models. Fig. 3 includes fragments of the isotherms of adsorption at 773 K for these models. As it can be seen, the amount of platinum exerts an influence on the adsorption of *n*-heptane, but this is not as distinct as that of temperature or pressure. With models of a higher Pt-content, there is a slight increase in the number of adsorbed molecules. It can, therefore, be

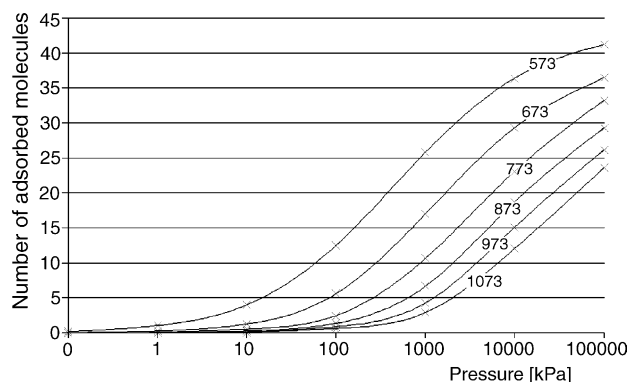


Fig. 2. Isotherms of adsorption of *n*-heptane on Pt/γ-Al₂O₃ related to temperature (model with seven Pt atoms 1.43 wt.%).

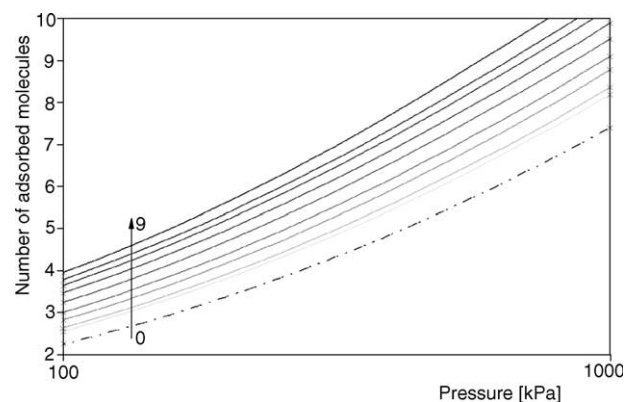


Fig. 3. Isotherms of adsorption of *n*-heptane on Pt/γ-Al₂O₃ for increasing Pt content (773 K).

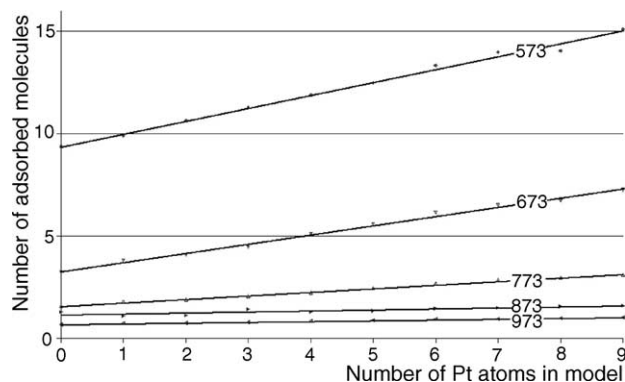


Fig. 4. Number of adsorbed *n*-heptane molecules related to Pt content (573–973 K; 100 kPa).

anticipated that the presence of platinum favorably affects *n*-heptane adsorption. As the content of the noble metal increases, so does the amount of the hydrocarbon in the catalyst pore. The plot presenting the isotherm for the model where Pt is absent noticeably differs from the remaining curves.

Fig. 4 relates the number of adsorbed *n*-heptane molecules to the Pt content of the models at a constant pressure of 100 kPa and varying temperature. As shown by these plots, the number of adsorbed molecules rises linearly with increasing metal content, irrespective of the temperature applied. We may, therefore assume that the effect of the substituted Pt atoms is an additive one. Fig. 4 also shows that the influence of the metal content decreases with increasing temperature.

The plots relating the number of *n*-heptane molecules adsorbed to the pressure applied have a different shape. Fig. 5 shows the adsorption isotherms for the Pt-containing catalyst models which differed in the configuration of the noble metal atoms. Thus, adsorption in the catalyst model with a Pt particle is facilitated as compared to that in the model of an equivalent Pt content when the pressures of the lower investigated range are applied. Over the higher investigated pressure range, the adsorption of *n*-heptane

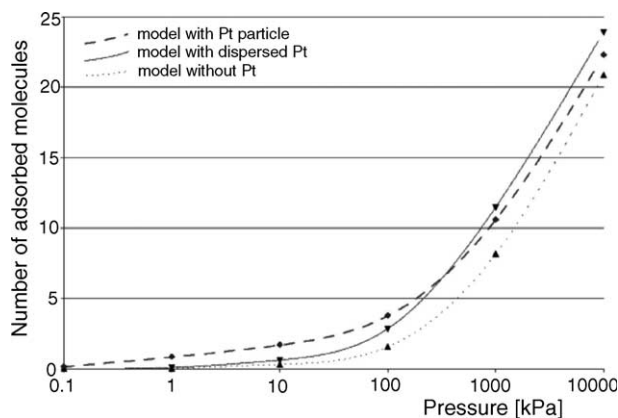


Fig. 5. Isotherms of adsorption on catalyst models differing in the arrangement of Pt atoms.

molecules is facilitated in the model with platinum totally dispersed. However, adsorption is visibly hindered in the support model where Pt is absent, regardless of the process conditions applied.

It seems interesting to compare the slopes of the straight lines which relate the number of adsorbed molecules to the Pt content, calculated for the different temperatures and pressures of adsorption. It may be assumed that the higher is the slope at a given temperature and pressure, the greater is the role of platinum in facilitating adsorption under these conditions.

Fig. 6 shows the isolines of the slopes of the straight lines illustrating the effect of Pt on adsorption, approximated with quadratic polynomial for different simulation conditions. In this way 10 isolines were plotted. As shown by these isolines, the favorable contribution of platinum is the most pronounced at 573 K and approximately 100 kPa. With pressure lower or higher than 100 kPa, the effect of Pt becomes weaker (the slopes of the straight lines decrease). A rise in temperature impairs the role of platinum in facilitating adsorption (the slopes decrease), and the maximums of the slopes shift towards higher pressure values when the temperature increases.

The approximation of the slope values with a quadratic polynomial is of a qualitative rather than quantitative nature because of a comparatively low correlation coefficient ($R = 0.710$). It may, however, be expected that the favorable effect of Pt which facilitates adsorption will further increase with the drop in temperature.

Comparison of calculated and experimental data raises problems for two reasons. One of these is the highly irregular structure of the material. The porous structure of the model adopted for the calculations consisted of an infinite number of parallel micropores, which do not intersect. A structure like this is far from representing the real porous structure of γ - Al_2O_3 , so it did not seem useful to make direct comparisons with experimental data. On the other hand,

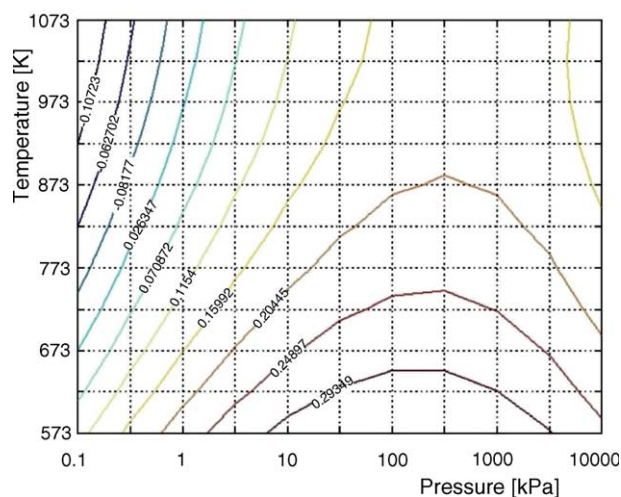


Fig. 6. Effect of Pt content in the catalyst model on the adsorption equilibrium in the *n*-heptane–Pt/ γ - Al_2O_3 system.

if we had constructed a model better reflecting a real structure, this would have failed to be successful because of the size limitations imposed by the duration of the simulation procedure.

The other reason why the comparison of calculated and experimental data becomes infeasible is the reactivity of the Pt-containing system. Under conditions corresponding to those of simulation, there would soon be established an equilibrium state between the reagents in the catalyst interior, thus making impossible any examination of the adsorption equilibrium for particular reagents.

Taking these into account, we decided that our study should be solely of a theoretical character.

4. Summary

Using the molecular modeling method, the effect of platinum on the adsorption of *n*-heptane on the Pt/ γ -Al₂O₃ catalyst was determined. The plots of the adsorption isotherms imply that the number of the hydrocarbon molecules adsorbed increases with the weight percent of the noble metal in the catalyst. This increase is directly proportional to the Pt content at each of the temperatures and pressures applied. The favorable effect of platinum is the most distinct at 573 K and 100 kPa.

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