

# Energetically preferred locations of hydrocarbons in the structure of a Pt-Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst: docking method

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## Abstract

The use of methods dealt with in computational chemistry for the design of efficient catalysts has become increasingly frequent. In our study, molecular modeling methods were used to find the catalytic sites of a Pt-Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Five different catalyst models including one support model were constructed. With the docking method, the most probable locations of hydrocarbon molecules on the micropore surface were determined. The host–guest interaction energy was calculated for all locations, using the CVFF approach. The results revealed a very strong influence of the platinum centers and a considerably weaker one of the tin centers, comparable to those of the support atoms. Calculations were also carried out to establish the distance of the adsorbed hydrocarbon molecules from the catalyst model—the distance of the shortest contact. Aliphatic hydrocarbons adsorb much closer to the micropore surface than do cyclic hydrocarbons.

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## 1. Introduction

Adsorption of molecules in solids is part of the catalytic process which occurs in the catalyst grain. As a result, the molecules of a substance (adsorbate) are bound to the surface of another molecule (adsorbent). This should be attributed to the nonsaturation of the solid surface, which then exhibits an excess of free energy as compared to the bulk [1]. There are two types of adsorption: physical adsorption, where the adsorbate molecules are bound to the adsorbent (catalyst) surface by the molecular interaction forces of van der Waals type, and chemisorption, where chemical bonds between the interacting molecules are formed. The adsorbed molecules can be located at certain sites, i.e. the active centers on the adsorbent surfaces. The energetically favorable locations and interaction energy are a prerequisite for the understanding of the adsorbing and catalytic properties of the Al<sub>2</sub>O<sub>3</sub> systems. Heterogeneous catalysts are solids differing in composition and in the arrangement of atoms. The catalytic centers are generally defined as inhomogeneities in

the crystal lattice, e.g. as lattice defects or the presence of heteroatoms.

Highly dispersed platinum catalysts and platinum-containing bimetallic catalysts are widely used for naphtha reforming [2]. The first Pt–Re-promoted catalysts appeared in the 1960s [3], and since then, a number of other bimetallic catalysts have been developed for industrial uses [4]. There are two groups of bimetallic catalysts used in naphtha reforming. One of these (Pt–Re and Pt–Ir belong there) comprises catalysts whose activity is comparable to that of the monometallic Pt catalyst [5], but they can be used at lower pressure. The other group includes catalysts which are less active than those of the first group, but they provide increased stability. From this group, tin catalysts are more widely used.

In a catalyst, tin is present in many different forms. Dautzenberg et al. [6] studied *n*-hexane conversion over Pt–Sn-supported alumina and silica. They found Pt–Sn alloys on silica and tin oxide on the alumina support. This, however, depends on the preparation technique used.

The role of tin is still controversial. Burch and Garla [7,8] reported that tin modifies both the acidity of the support and the electronic properties of platinum, the main effect being the reduction of catalytic activity in the coking reactions.

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Arteaga et al. [9] concluded that those changes were caused by the geometric effects of tin-blocking Pt sites rather than by the electronic effect.

## 2. Scope of the investigations

The catalyst under study was a Pt-Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-reforming catalyst, which adsorbed the reagents of the reforming process on its surface at the first stage of the reactions involved. The aim of the study was to find the potential active centers of the catalyst to assess the location of one or more molecules of the adsorbate in the proximity of the centers, as well as to estimate the energy of the system in the adsorbent molecule positions which have been found. These goals were achieved using computer simulations of the behavior of the host–guest system on the molecular interaction level. The tool which made it possible to determine the energetically advantageous positions of organic molecules in the catalyst structure was a combination of the stochastic Monte Carlo (MC) method and the deterministic molecular dynamics (MD) approach. Such combination is referred to in the literature as the docking method [10] and it has the advantage of allowing the location of the active centers in the catalyst to be determined and the energy of the system in the preferred sites of adsorption to be calculated. All the information is very useful when the catalysts under design have to perform more effectively.

## 3. Model and computational details

### 3.1. The model of Pt-Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

The construction of an appropriate model is a key issue in each computer simulation that aims at visualizing the behavior of a real system. The structure of the model should be sufficiently simple to eliminate the influence of any undesired factors and to yield unequivocal results. If the model is small in size, this will minimize the calculating costs. On the other hand, to make the simulation meaningful, we must not allow the catalyst model to differ very much from a real catalyst. Hence, to meet these requirements, the following operations had to be performed:

- For the needs of this study, we built a model consisting of 64 elementary cells ( $4 \times 4 \times 4$ ). There, by removing relevant atoms, we placed a cylindrical 18 Å diameter micropore. Aluminum oxide has a crystalline structure, and its elementary cell is a cubic of an 8.4 Å side. However, its structure was too small to meet the requirements of the simulation.
- For the needs of the simulation procedure, five support/catalyst models differing only in the content and locations of the metals (Pt and Sn) were prepared. Model 1 was the catalyst support. Models 2 and 3

contained Pt (three atoms—0.98%) and Sn (three atoms—0.60%), respectively. Models 4 and 5 contained both Pt and Sn, but their locations were different. Such choice made it possible to determine how the presence of a particular metal affected the locations of potential adsorption centers and the host–guest interaction energies.

- Metal atoms were connected to the support by oxygen bridges [9]. After each modification of the catalyst model, the geometry of the support model was optimized.
- The models prepared via the above route differed only in the arrangement of metal atoms. In this way, it was possible to eliminate the effect of some factors (e.g. micropore diameter, difference in the arrangement of the support atoms) on the results of simulation.
- The adopted adsorbate models were hydrocarbons with seven carbon atoms: heptane, 3-ethylpentane, methylcyclohexane and toluene.

Models used in simulations are shown in Fig. 1.

### 3.2. Algorithm of the docking method

Docking simulations were carried out using the procedure proposed by Freeman et al. [10,11]. The realization of the algorithm can be divided into three steps involving different computational techniques of molecular modeling.

The first step includes the simulation of the molecular dynamics of an isolated hydrocarbon molecule with the aim to prepare a set of conformations for the molecule. This step was carried out with two aliphatic hydrocarbons, *n*-heptane and 3-ethylpentane, which are able to generate a large number of conformers owing to their flexibility. The adopted simulation temperature was 1000 K because the aim was to obtain the largest possible set of potential conformers. The duration of the simulation procedure was set to 10 ps; after every 1 ps, the current coordinates of the atoms were recorded in the trajectory file. In this way, a library of 10 conformers was obtained for each molecule. With methylcyclohexane and toluene, this step was omitted; because of their ring structure, the molecules of these hydrocarbons are much more rigid and therefore less ready to generate conformers.

The second step involves molecule docking, which is performed using the MC method. Each detected conformer of the hydrogen molecule is placed at a random site within the supercell of the catalyst. Only configurations with interaction energies lower than the anticipated threshold values are accepted for further optimization. The threshold values for each hydrocarbon molecule were appropriately chosen so as to find several potential adsorption sites of the lowest energy. The docking procedure was repeated 10 times with those molecules for which no search of conformers had been carried out, in order to find an easy way for the comparison of the simulation results.

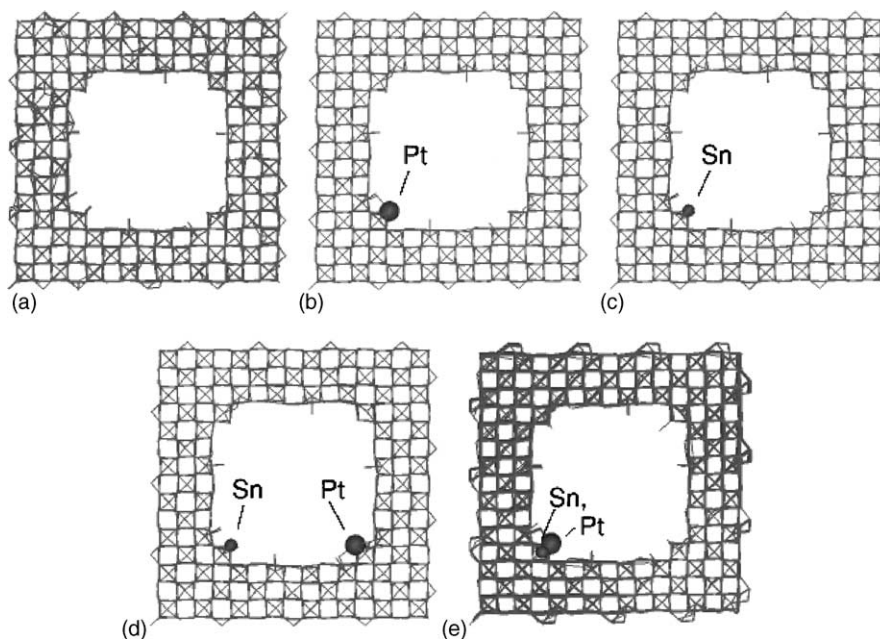


Fig. 1. Models of the catalysts used in the simulations: (a)  $\gamma$ - $\text{Al}_2\text{O}_3$  support; (b)  $\gamma$ - $\text{Al}_2\text{O}_3$  with Pt atoms; (c)  $\gamma$ - $\text{Al}_2\text{O}_3$  with Sn atoms; (d)  $\gamma$ - $\text{Al}_2\text{O}_3$  with Pt and Sn atoms located on the opposite sides of the micropore; and (e)  $\gamma$ - $\text{Al}_2\text{O}_3$  with Pt and Sn atoms located on the same side of the micropore.

The third step includes minimization of the energy of docked structures by optimizing the arrangement of the host atoms and guest atoms with respect to one another. Consequent to our previous work [12], use was made of the CVFF [13–20], with additional parameters for Pt taken from Halioglu et al. [21].

## 4. Results and discussion

### 4.1. Location of molecules

Figs. 2–6 show the location of the adsorbate molecules inside the micropore of the investigated system. It is worth

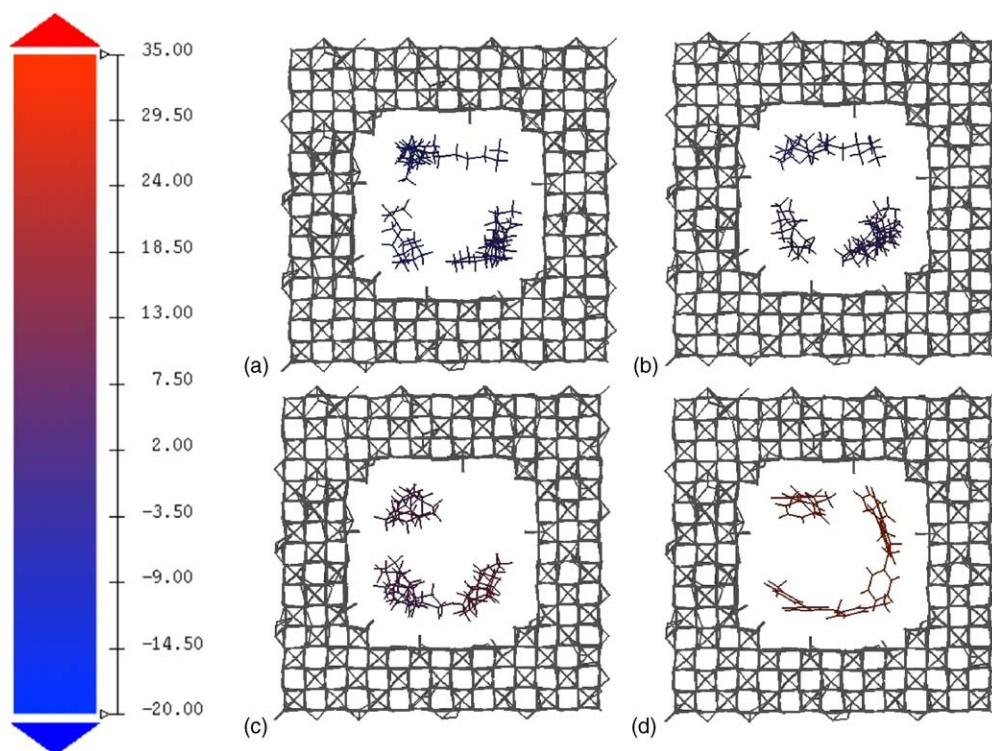


Fig. 2. Location of hydrocarbon molecules: (a) heptane; (b) 3-ethylpentane; (c) methylcyclohexane; and (d) toluene, in  $\gamma$ - $\text{Al}_2\text{O}_3$  support.



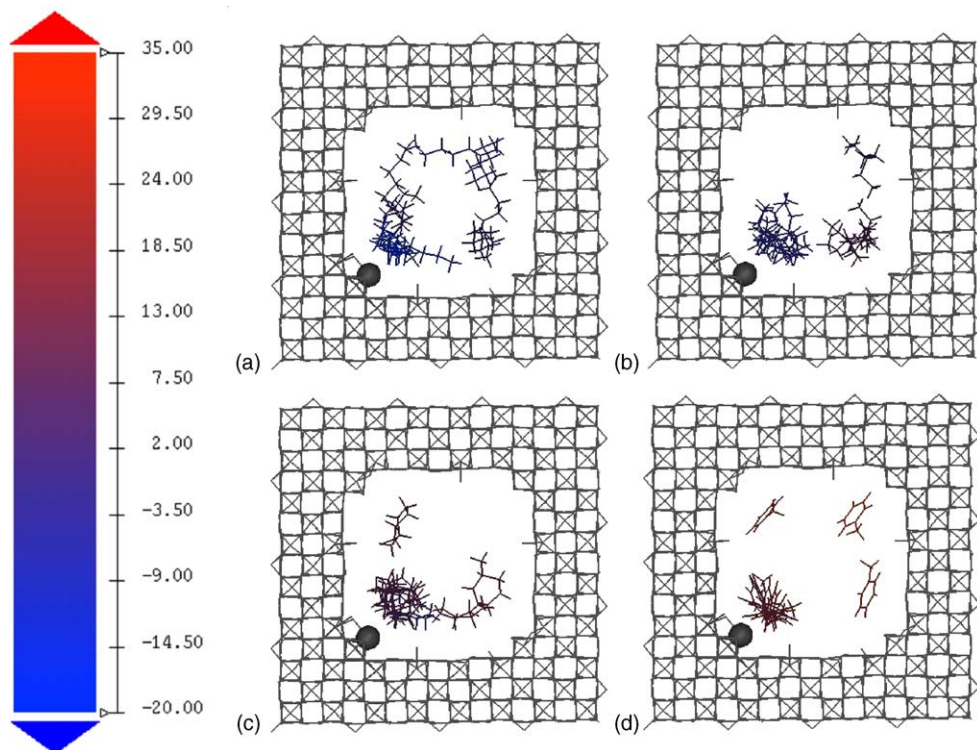


Fig. 3. Location of hydrocarbon molecules: (a) heptane; (b) 3-ethylpentane, (c) methylcyclohexane; and (d) toluene, in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with Pt atoms.

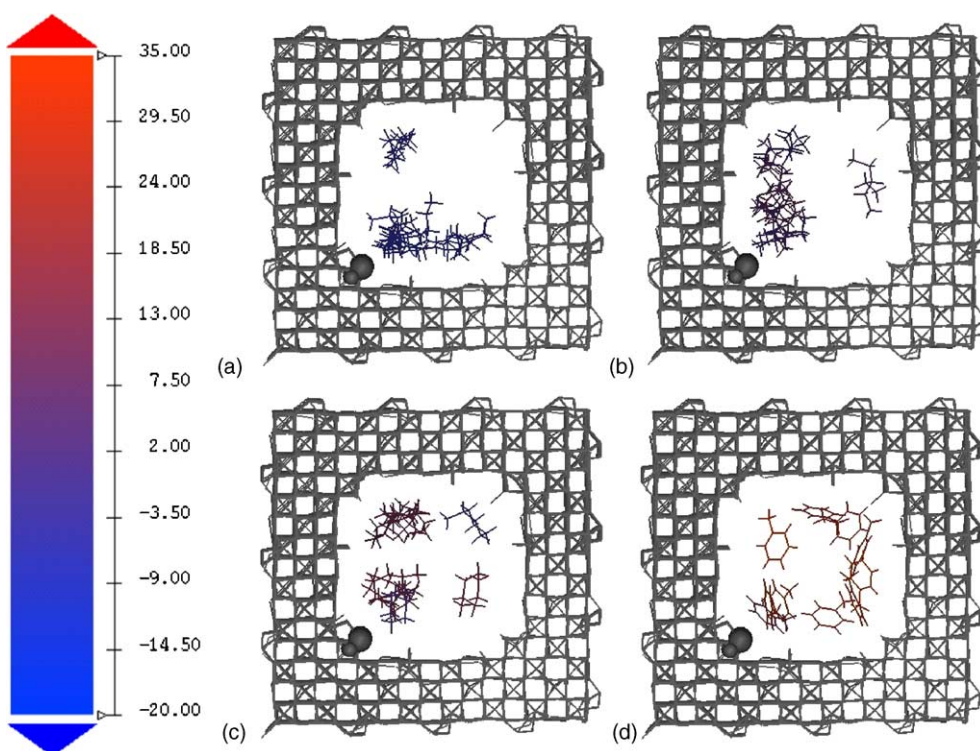


Fig. 4. Location of hydrocarbon molecules: (a) heptane; (b) 3-ethylpentane; (c) methylcyclohexane; and (d) toluene, in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with Sn atoms.

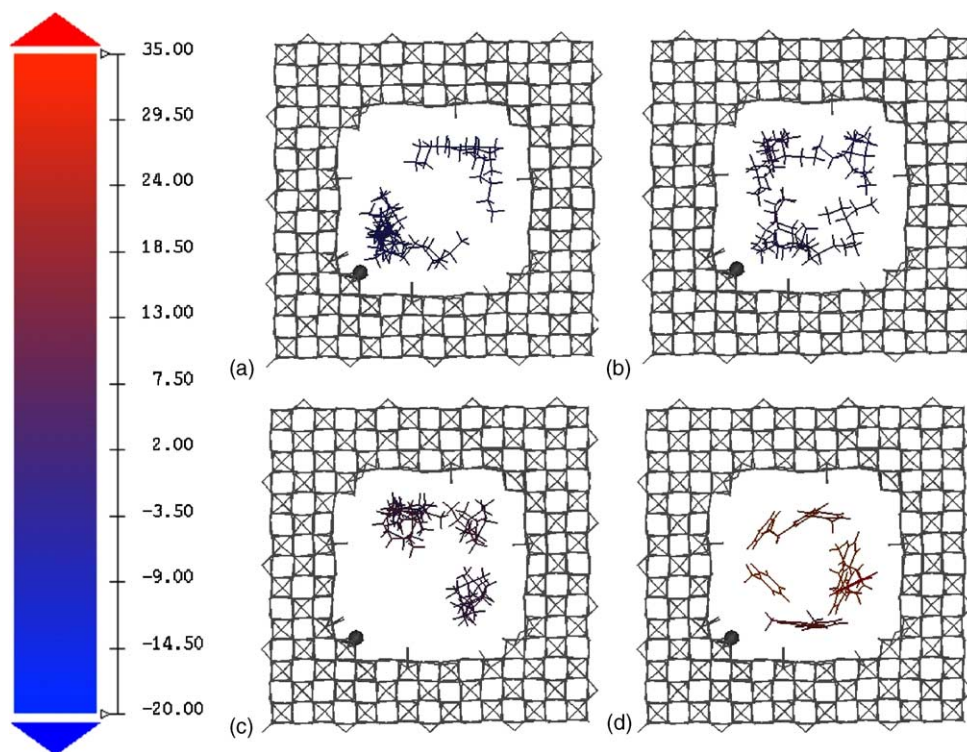


Fig. 5. Location of hydrocarbon molecules: (a) heptane; (b) 3-ethylpentane; (c) methylcyclohexane; and (d) toluene in  $\gamma$ - $\text{Al}_2\text{O}_3$  with Pt and Sn atoms located on the same side of the micropore.

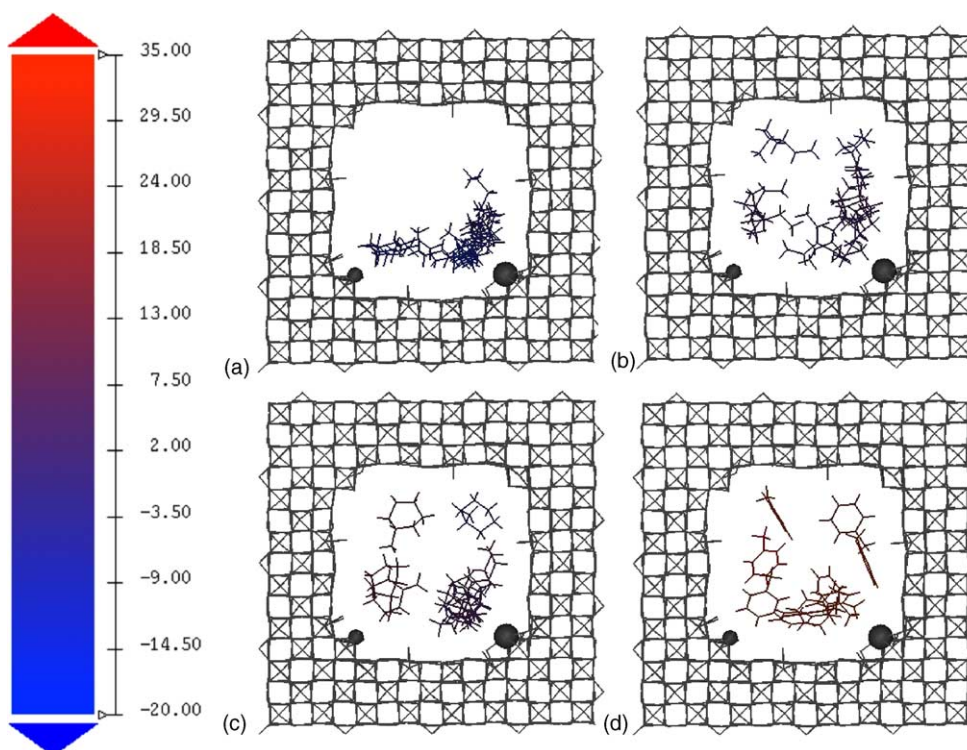


Fig. 6. Location of hydrocarbon molecules: (a) heptane; (b) 3-ethylpentane; (c) methylcyclohexane; and (d) toluene, in  $\gamma$ - $\text{Al}_2\text{O}_3$  with Pt and Sn atoms located on opposite sides of the micropore.

pointing to the fact that the hydrocarbon molecules are attracted to the micropore walls. The molecules adsorb at a small distance from the walls; they do not occur in the central part of the micropore—close to its axis. This holds for all of the investigated systems, irrespective of hydrocarbon or the presence and arrangement of heteroatoms in the catalyst.

With the  $\text{Al}_2\text{O}_3$  support model without metal atoms (Fig. 2), it can be observed that the molecules adsorb at the characteristic teeth situated in the micropore corners. This should probably be attributed to the advantageous arrangement of the aluminum oxide atoms. The difference in energy for particular adsorption sites may even amount to over a dozen kilocalories per mole, for example, with methylcyclohexane.

With the platinum-containing model (Fig. 3), it is clearly seen that the hydrocarbon molecules adsorb close to the platinum centers, but they also adsorb at other sites, though they are most likely to be found in the proximity of atoms.

A similar behavioral pattern is observed with the model where platinum and tin are located close to each other (Fig. 6). As it can be seen, hydrocarbon molecules accumulate in the vicinity of metal atoms, except for toluene (Fig. 6d), where no preferred adsorption site in the micropore interior is observed.

The influence of the tin centers (Fig. 4) is not as clear as that of the platinum sites. While heptane molecules are attracted to the vicinity of the tin centers, 3-ethylpentane molecules are arranged uniformly throughout the available space, and there is no distinct preference of adsorption cen-

ters. Toluene follows a similar pattern. Methylcyclohexane does not adsorb in the proximity of the tin centers, but this probably is not due to the repellent interaction of tin. On comparing the arrangement of the hydrocarbon molecules in the models with no heteroatoms (Fig. 2) and their arrangement in the model with tin atoms (Fig. 4), it can be inferred that the type and extent of tin interaction are comparable with those of the interactions resulting from the defects of the  $\text{Al}_2\text{O}_3$  structure. Hence, the influence exerted by tin does not markedly contribute to the arrangement of the docked molecules.

What raises interest is the distribution of hydrocarbons inside the micropore of the model where both heteroatoms are located at a certain distance from each other (Fig. 5). The attracting interactions of platinum noticeably prevail over the interactions of tin in the case of heptane. Although 3-ethylpentane is scattered throughout the micropore, its molecules can often be found in the proximity of the platinum centers. Similar behavior was traced for methylcyclohexane (to a greater extent) and toluene (less frequently). If we were to regard the interactions of tin as repellent ones, then—taking into account the attracting interactions of platinum with respect to methylcyclohexane (Fig. 3c)—we should expect an enhancement of these interactions in the model containing both heteroatoms in different corners of the micropore. However, the arrangement of the hydrocarbons in the micropore is similar to that in the model which contains platinum alone. In this context, there seems to be the probability that the influences of tin and of the support atoms on adsorption are of similar intensity.

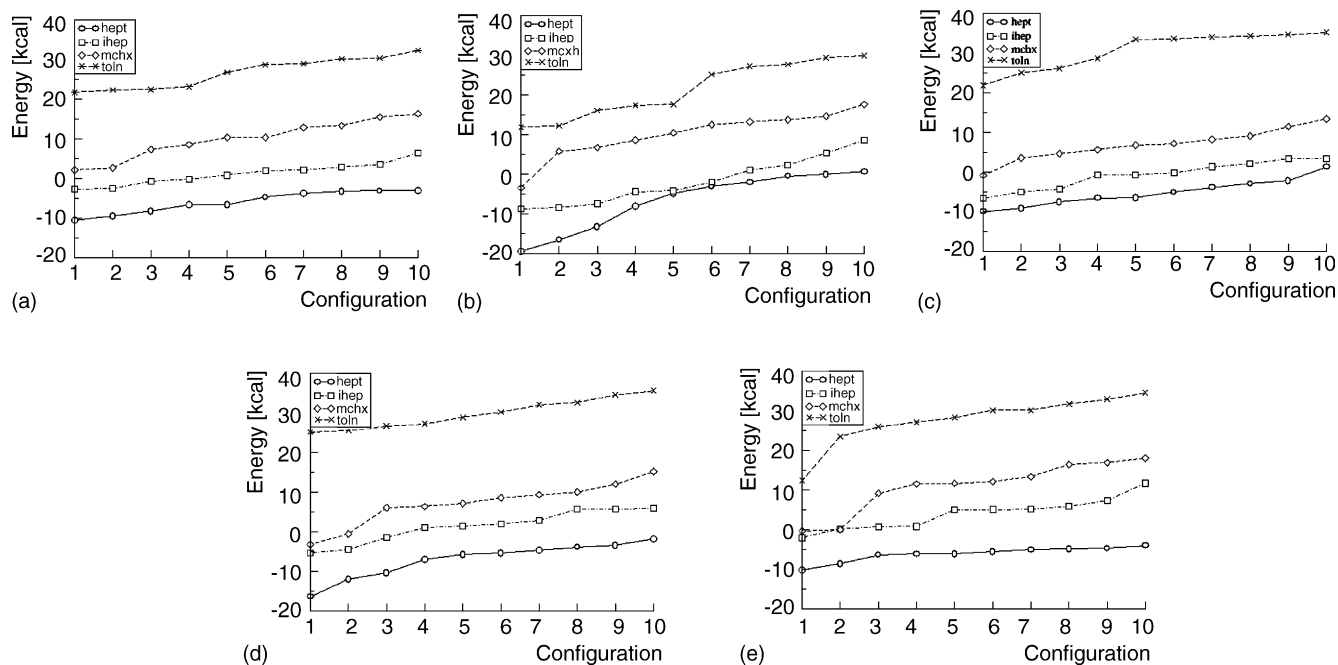


Fig. 7. Docking energy for (a)  $\gamma\text{-Al}_2\text{O}_3$  support; (b)  $\gamma\text{-Al}_2\text{O}_3$  with Pt atoms; (c)  $\gamma\text{-Al}_2\text{O}_3$  with Sn atoms; (d)  $\gamma\text{-Al}_2\text{O}_3$  with Pt and Sn atoms located on the opposite sides of the micropore; and (e)  $\gamma\text{-Al}_2\text{O}_3$  with Pt and Sn atoms located on the same side of the micropore.



Table 1  
Average energies of docked structures (kcal/mol)

Model	Heptane	3-Ethylpentane	Methylcyclohexane	Toluene
Al <sub>2</sub> O <sub>3</sub> (Fig. 1a)	-5.93	1.55	9.93	26.69
Pt/Al <sub>2</sub> O <sub>3</sub> (Fig. 1b)	-6.71	-1.76	9.98	21.45
Sn/Al <sub>2</sub> O <sub>3</sub> (Fig. 1c)	-5.22	-0.73	6.93	30.73
Pt-Sn/Al <sub>2</sub> O <sub>3</sub> (Fig. 1d)	-7.04	1.34	7.1	29.83
Pt-Sn/Al <sub>2</sub> O <sub>3</sub> (Fig. 1e)	-6.14	3.99	10.89	27.65

#### 4.2. Host-guest interaction energy

With each of the models used, we observed a certain pattern. Fig. 7 shows that in the analyzed models, the interaction energies for the most advantageous locations of the adsorbates range between the following values: with heptane, from about -20 to about 0 kcal; with 3-ethylpentane, from about -9 to about 5 kcal; with methylcyclohexane, from about -3 to about 15 kcal; and with toluene, from about 12 to about 35 kcal. Thus, we can establish the following sequence of ascending order for the interaction energies:

$$E(\text{heptane}) < E(3\text{-ethylpentane}) \\ < E(\text{methylcyclohexane}) < E(\text{toluene})$$

These findings show that, irrespective of the catalyst model used, heptane has the greatest ease to adsorb because of its very low interaction energy. Toluene desorbs from the adsorption centers because the interaction energy takes a positive value.

Table 1 gathers the mean energies of hydrocarbon interactions with particular catalyst models. The analysis of these values allows the following generalizations to be made: heptane, 3-ethylpentane and toluene show the strongest interaction with the platinum catalyst (Fig. 3) and methylcyclohexane with the catalyst containing tin alone (Fig. 4). Strong interactions are also found to occur in the bimetallic catalyst models, but the interaction with hydrocarbons is slightly stronger in the model where the Pt and Sn atoms are located on the opposite sides of the micropore.

#### 4.3. Shortest contact

It seemed worthwhile to compare the shortest interatomic distances in the interacting host-guest molecules (Fig. 8). Thus, there is a clear difference in the distance from the adsorption center between aliphatic hydrocarbons and cyclic hydrocarbons. While this distance is very short with heptane and 3-ethylpentane, amounting to approximately 0.5 Å, it increases to about 2.5 Å with methylcyclohexane and toluene. The fact that the hybridization of the carbon atoms in methyl-

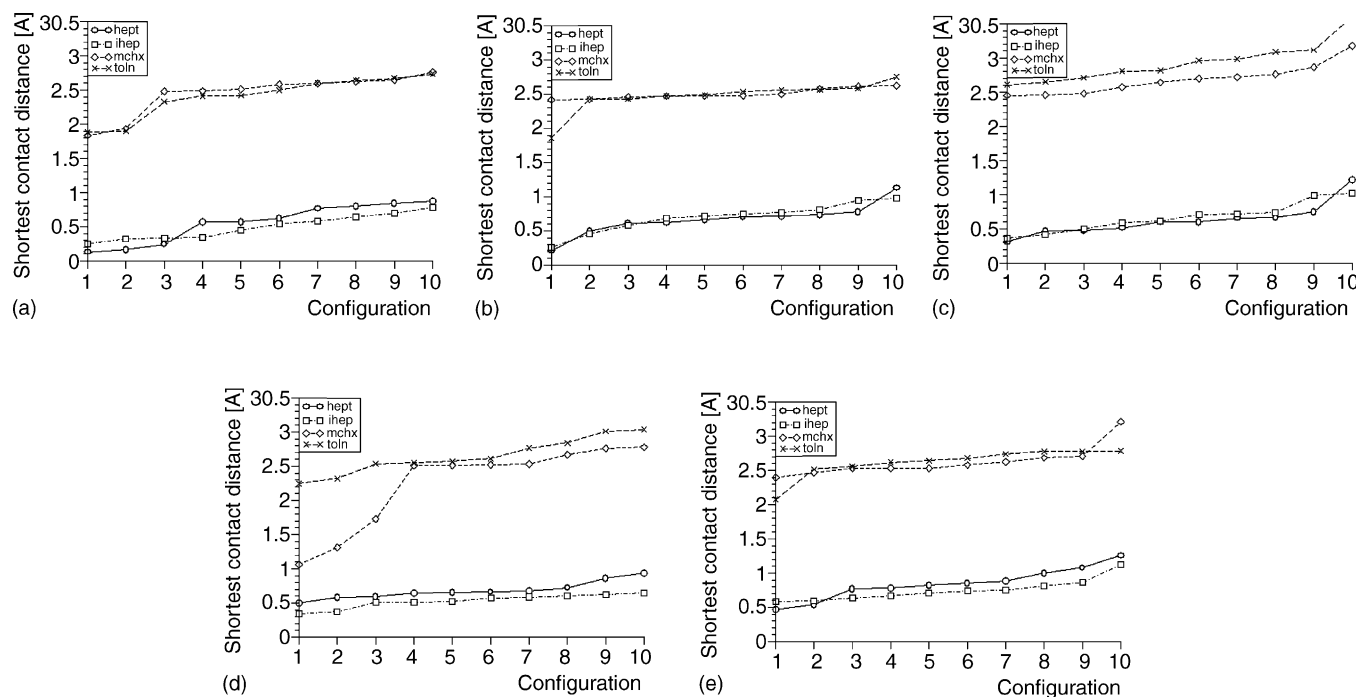


Fig. 8. Shortest contact distance for (a)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support; (b)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with Pt atoms; (c)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with Sn atoms; (d)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with Pt and Sn atoms located on the opposite sides of the micropore; and (e)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with Pt and Sn atoms located on the same side of the micropore.

Table 2  
Average shortest contact distance (Å)

Model	Heptane	3-Ethylpentane	Methylcyclohexane	Toluene
Al <sub>2</sub> O <sub>3</sub> (Fig. 1a)	0.56	0.49	2.45	2.41
Pt/Al <sub>2</sub> O <sub>3</sub> (Fig. 1b)	0.67	0.7	2.5	2.47
Sn/Al <sub>2</sub> O <sub>3</sub> (Fig. 1c)	0.63	0.67	2.68	2.93
Pt–Sn/Al <sub>2</sub> O <sub>3</sub> (Fig. 1d)	0.67	0.53	2.24	2.65
Pt–Sn/Al <sub>2</sub> O <sub>3</sub> (Fig. 1e)	0.85	0.75	2.63	2.62

cyclohexane is the same as the one in the aliphatic hydrocarbons (sp<sup>3</sup>) and, consequently, the spatial arrangements of the C and H atoms are similar without any meaning here.

Toluene molecule contains C atoms with sp<sup>2</sup> hybridization and adsorbs in such a way that the aromatic ring is parallel to the micropore walls (Figs. 2d–6d). In that particular case, the shortest contact is noticeably greater than that in the aliphatic hydrocarbon molecules and comparable with that of methylcyclohexane.

Table 2 includes the average interatomic distances (of 10 conformers of hydrocarbon) in the active metal (active center) and the adsorbate (hydrocarbon). The comparison of the average host–guest distances in the different support models shows that the shortest contact is the one in the Al<sub>2</sub>O<sub>3</sub> (Fig. 1a) support (Table 2). Methylcyclohexane is an exception; for this hydrocarbon, the shortest contact is with the Pt–Sn/Al<sub>2</sub>O<sub>3</sub> (Fig. 1d) model, where Pt and Sn are located in two different corners of the micropore. For the aliphatic hydrocarbons, the farthest distances are found in the Pt–Sn/Al<sub>2</sub>O<sub>3</sub> (Fig. 1e) model with Pt and Sn in the same corner. The shortest contact distances for methylcyclohexane are comparable with one exception; this is the Pt–Sn model mentioned, where the distance distinctly shortens from about 2.5 Å to about 1 Å (Fig. 8). For toluene, the farthest distances of contact occur in the catalyst model containing Sn alone (Table 2).

## 5. Conclusions

The results of the study allow the following conclusions to be drawn about the interaction of C<sub>7</sub> hydrocarbons with the Al<sub>2</sub>O<sub>3</sub> models:

- The application of the docking method to a variety of catalytic systems has revealed that inhomogeneities of the Al<sub>2</sub>O<sub>3</sub> crystal lattice (e.g. platinum or tin atoms or a specific arrangement of atoms in the support) act as adsorption centers, with a distinct dominance of platinum interaction over the other inhomogeneities.
- The strongest adsorption is that of the heptane molecules; the weakest is that of toluene.
- The measured distances from the adsorption center are arranged in following sequence: aliphatic hydrocarbons adsorb at the shortest distance (approximately 0.5–1.0 Å)

and cyclic hydrocarbons at the farthest distance (about 2.5 Å). The hybridization of the carbon atom in the ring is without any meaning.

- The aromatic ring of toluene adsorbs parallel to the micropore walls.

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