GCMC simulations of CO_2 adsorption on zeolite-supported Ir_4 clusters

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ABSTRACT

We have studied the adsorption of CO_2 molecules inside the pores of faujasite zeolite and evaluated the influence of the Ir_4 clusters on the intensity of the adsorption. The force field designed for CO_2 adsorption in zeolites has been extended with the parameters for the CO_2/Ir_4 interactions, taking the Density Functional Theory (DFT) energies as a reference. We have found that despite the fraction of the pore volume that is occupied by the Ir_4 cluster, the adsorption is more intense than that of empty faujasite. The adsorption sites next to the cluster are very characteristic, and the interactions are more intensive due to the interactions of zeolite and the Ir cluster both playing an important role.

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1. Introduction

Global interest in carbon dioxide utilization is a result of significantly increasing amounts of CO_2 in the atmosphere and dynamically rising emissions of this greenhouse gas. Because the majority of CO_2 comes from carbon-based energy production and contributions of other energy sources do not appear to be expanding in the near future, it is predicted that this trend will stay unchanged [1,2].

Many solutions to decreasing carbon dioxide emissions have been proposed, including capture and sequestration [3], but a better solution appears to be chemical conversion into more valuable products through the use of specially designed catalysts. At present, chemical conversion can only reduce the amount of emission by a small percentage as the total amount of carbon emission is too large. For this reason, development of highly active and selective catalysts for conversion of CO_2 into highly demanded products (e.g., fuel components) is the point of particular interest.

Zeolites are reported to be one of the promising material groups for carbon dioxide capture because of their selectivity and high capacity. It is known that these properties can be tuned by the Si/Al ratio to correlate directly with the acidity of zeolites. The introduction of extra-framework metal cations or clusters [4] might also increase the catalytic activity of pure zeolites. Kim et al. [5] have screened many zeolite structures and MOFs with respect to their CO_2-capture capabilities. These authors present a list of 20 zeolites that are recommended to be investigated with high priority for use in carbon-capture applications. According to the list, faujasite

(FAU), tschortnerite (TSC) and RWY zeolite are the most promising structures.

Because the catalytic conversion of CO_2 is more in demand compared with sequestration, a carbon-capture material should be able to act as the catalyst for CO_2 hydrogenation to obtain more useful products. This step is difficult due to the very high stability of the CO_2 molecule; however, many potential catalysts have been suggested. An extensive review of the methods for carbon dioxide utilization was presented by Razali et al. [6], Wang et al. [2] and Aresta et al. [1].

A large variety of methods for CO_2 conversion has been discussed, e.g., CO_2 reforming of CH_4 [7,8], synthesis of carbon monoxide, conversion to methanol [9] and ethanol [10,11] and production of dimethyl ether. [12]

The modified Fischer–Tropsch process, which makes use of CO_2 instead of CO, has been proposed as a means of synthesizing hydrocarbon fuels [13]. At the same time, it was confirmed experimentally that faujasite-supported rhodium clusters are active in the hydrogenation of carbon monoxide to hydrocarbons [14].

Several potential catalysts have been proposed, including metal surfaces, [15] but the acidic sites of zeolites [16] are presumably the easiest to employ, due to the abundance of commercial zeolites that are available. Because the hydrogenation of carbon dioxide is a redox reaction, metal-containing zeolites can be good candidates for catalysts. [17]

Hydrogen spillover process on the metal clusters (especially tetrairidium) supported on zeolites has been proposed by Rösch [18,19], to be the reducing agent for the hydrogenation. Clusters of various metals and of various sizes can be used in the process, which allows fine tuning of the process conditions. This approach, however, raises the issue of the adsorption capabilities of such clusters, because the ability of the metal cluster to generate the hydrides out

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of the H_2 molecules is as essential in this process as the ability to activate the CO_2 molecule.

The structure and (catalytic) properties of the metal clusters in zeolites have been widely studied by the group of Gates [20–22], who indicated that the supported metal clusters are highly reactive while the same support remains weakly reactive, and this is, therefore, a promising avenue by which to obtain active and selective catalysts.

2. Aim of the study

In this study, we have selected one of the proposed systems, namely, a tetrairidium cluster supported by faujasite [4,23,24], to investigate its adsorption properties toward CO_2 molecules.

We intended to investigate carbon dioxide adsorption capabilities of faujasite-supported tetrairidium clusters by using a specially designed forcefield for CO_2 adsorption on zeolites, which was modified for the purposes of this work to allow interactions between the Ir and CO_2. The resulting forcefield combines the advantages of the Garcia-Sanchez forcefield, such as the transferability to all zeolite frameworks and the ability to provide trustworthy results, with the parameters for iridium clusters to describe the interactions between CO_2 and the clusters.

Making use of this forcefield, we intended to gain insight into the adsorption process. The adsorption sites and the influence of the Ir on the curves of the adsorption isotherms were of particular interest.

3. Model and computational details

The GCMC method has been widely used in simulations of adsorption for decades [5]. Obviously, as is the case in all simulations, the quality of the results depends on the potential used, and to obtain meaningful results, a proper description of the energy of the system is necessary.

There are many forcefields that are available that have been parameterized for the adsorption of small (organic) molecules in zeolites [25]; CO_2 molecules, however, are particular in terms of their interactions.

Recently, a new forcefield has been developed [26] that is capable of giving exceptionally good results in terms of the adsorption isotherms of CO_2 in zeolites. The authors claim that this forcefield is transferable to all zeolite frameworks. For these reasons, we have decided to use this forcefield, enhanced by parameters for Ir_4 cluster from DFT simulations. We have implemented the forcefield in Accelrys Materials Studio 6.1, to be used with the Sorption module.

3.1. Forcefield fitting

The forcefield described in the original paper includes only the interactions between specific pairs of atoms (off-diagonal terms). The interactions taken into account are both electrostatic and van der Waals; thus, the energy expression of this forcefield is the following:

$$E = \frac{q_1 \cdot q_2}{R^2} + D_0 \left[\left(\frac{R}{R_0} \right)^{12} - 2 \left(\frac{R}{R_0} \right)^6 \right] \tag{1}$$

Out of the forcefields available in the Materials Studio package, the Dreiding forcefield [27] uses the same expression for non-bonding interactions. For this reason, we have implemented all of the modifications in this forcefield, making sure that all of the original Dreiding parameters have been removed.

The atomic charges used are the integral part of the forcefield, and the charges of the metal clusters are not included in the original

paper. However, upon multiplication by 1.5 of the charges calculated with the Hirschfeld method for the zeolite atoms, we have obtained charges for Si, Al and O that closely matched those of the Garcia-Sanchez forcefield [26]. Therefore, we have decided to use this method to assign charges for the zeolite atoms and for the Ir cluster in our system to maintain consistency in the electrostatic effects in the system. The atomic charges for the CO_2 molecule were taken directly from the article. It has to be noted, that as far as the Ir cluster is concerned, the charges are smaller compared to the Si and Al atoms, and the electrostatic interactions are much weaker.

The second term in the energy expression is the Lennard-Jones term. The L-J parameters in the original forcefield are given for each pair of interacting atoms. These parameters have been added to the Materials Studio forcefield file after the unit conversion.

The only Lennard-Jones parameters for the Ir element available in literature to the best of our knowledge are for the surface diffusion of single Ir atoms on an Ir surface [28,29]. These parameters are not suitable for describing the interactions with the CO_2 molecules. Preliminary tests have shown that while the L-J component had a small negative value at the optimal distance, the sum of the L-J and electrostatic interactions were always positive, which means that only repulsion and not adsorption is possible.

Therefore, we have taken the task of fitting the parameters for the chemisorption of carbon dioxide on the Ir_4 cluster. To achieve this goal, DFT calculations were performed. For this purpose, the DMol^3 module was used. The optimal geometries were calculated and are shown in Fig. 1.

The distances between the Ir cluster and the chemisorbed CO_2 molecule, measured to the C and O atoms, are 2.1 Å and 2.9 Å, respectively. Importantly, the CO_2 molecule is bent, which differs
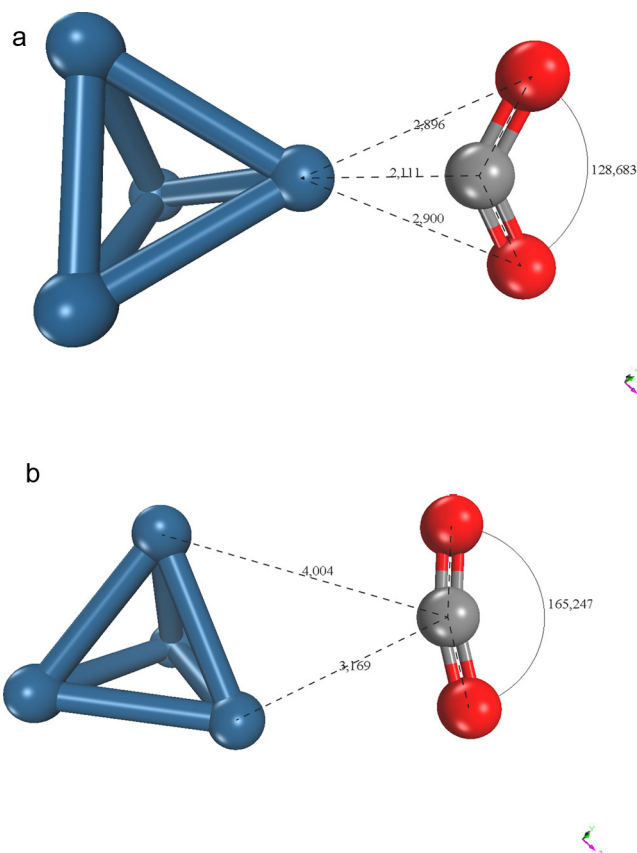

Fig. 1. Optimal geometries of CO_2 chemisorbed at the top of the Ir_4 cluster (a) and the transition state between minimums that correspond to the chemisorbed states (b).

from a linear conformation in the gas phase and corresponds to its activation.

Such bending of the CO_2 molecule needs special treatment in the fitting procedure. Our approach is based on the use of the linear CO_2 molecule for fitting – although reference DFT energies have been taken for the bent configuration. This approach leads to one particular site being occupied irrespectively on the bending of the CO_2 molecule, however, in both cases it has the same energy.

The only error that can be introduced by this approach is in high pressure runs, where there are more CO_2 molecules interacting with those already adsorbed on the Ir cluster, and small deviations in the geometry might play an important role when there is more CO_2 molecules present. To validate this, we have carried out additional simulations with all bent conformations and compared the results with simulations with all linear conformations. The results for simulations with bent configurations do not differ significantly with respect to linear. The adsorption sites are the same, the mass cloud shape is not substantially changed, as well as the energy pattern (edge sites more preferable than the top site) is maintained. It proves, that our approach of using linear configuration CO_2 molecule in the simulations does not affect the quality of the results.

To match the Lennard-Jones curve better, we have also disturbed the optimal geometry by moving the CO_2 molecule closer and farther relative to the optimal distance. The sum of the Ir_4 cluster energy and the CO_2 total energy was taken as a reference for the non-interacting molecules, what is equivalent to the molecules moved away to infinity. This approach ensures that the depth of the potential energy at the minimum is correct.

In addition, a selection of other configurations was also added to the list of fitted geometries. Most importantly, the configuration in which a CO_2 molecule was coordinated to the triangle, formed by the wall of the Ir_4 cluster. This configuration is not a thermodynamic minimum, and optimization of this geometry leads to the bent configuration on the top site. The GCMC scheme, however, relies on the random sampling of the geometries, and the proper simulation parameters of this unfavorable configuration should also be accounted for.

Three considered configurations require additional discussion. One of those configurations is the transition state between chemisorbed minimums, which is presented in Fig. 1b. The CO_2

molecule is slightly bent and is located parallel to the edge of the cluster. The calculated transition state is the barrier of the CO_2 transfer from one chemisorbed state (on the vertex) to the second state (on another vertex). The height of the barrier equals 13.6 kcal/mol.

The other structure that was considered is a configuration that is similar to the TS but rotated by 90 degrees, where CO_2 is perpendicular to the edge. This system is 0.6 kcal/mol more stable than the TS. Both configurations fit well to the other points that are included in the fitting.

In contrast, we have decided to reject a few configurations in which CO_2 was located closer to the cluster. The reason for this rejection is that the incorporation of this point to the fit introduces a significant error into the fitted potential. The closely located sites usually correspond to repulsive interactions, and the adsorption in this site is not likely to happen. On the other hand, it influences most of the preferred sites that have the strongest interaction energy. We have concluded that a proper description of the favorable geometries is more important than the repelling geometries, and accounting for these unfavorable structures in the fit is not desirable.

The fitting has been performed with an in-house developed Python program. This program took the initial set of parameters and fitted them to minimize the squares of the differences of the reference and calculated values. The initial parameters were taken to be the following: the $D_0(Ir–C)$ and $D_0(Ir–O)$ were set to the value of 15 kcal/mol, which is equal to the interaction between the CO_2 molecule and the Ir_4 cluster. The $R_0(Ir–C)$ was set to the distance from the top Ir atom to the C atom of the CO_2 molecule. The $R_0(Ir–O)$ was set to the distance between the O atoms of the CO_2 molecule and the Ir clusters that form the base of the tetrahedron. This arrangement allowed us to favor the CO_2 configuration adsorbed to the vertex, while the configuration on the wall would rather lead to the increased optimal distance in the physisorption region due to the oxygen atoms moving too close to the Ir atoms. This is most consistent with the reference DFT calculated values. The curves of the Ir–C and Ir–O interactions together with reference energy (DFT energy of Ir_4–CO_2 system) with respect to the distance are shown in Fig. 2.

The parameters obtained with the fitting method have been gathered in Table 1. Our scheme involves overbinding Ir–C interactions and repulsive Ir–O interactions for compensation. This choice
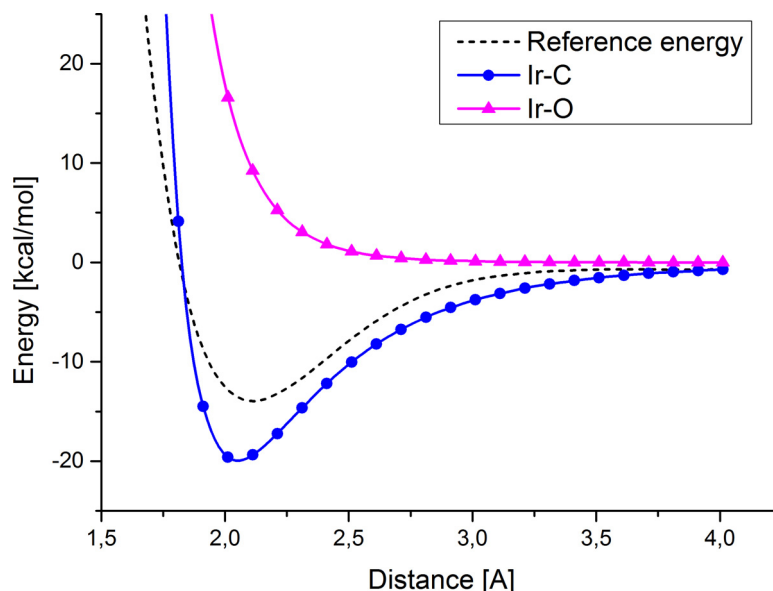

Fig. 2. The reference energy curve and the Lennard-Jones potential curves [kcal/mol] for the Ir-C (red) and Ir-O (blue) terms. For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.

Table 1
The Lennard-Jones parameters of Ir–C and Ir–O interactions.

	Ir–C	Ir–O
D_0 [kcal/mol]	19.8908	0.0009
R_0 [Å]	2.0526	4.5584

has been dictated by the geometry of the Ir_4 cluster (tetrahedron) that enables also the edge sites to be occupied by CO_2 molecules, and led to too strong adsorption on these sites due to the multiple Ir atoms taking part in the interactions. The repulsion introduced by the O atoms compensates this error and brings the energy values to the level of the reference DFT calculations. Admittedly, the fit to the reference curve (Fig. 3) is not perfect. There are far more electronic effects that are of importance when considering the interactions between the CO_2 molecule and the Ir_4 cluster which can be described by using a simple Lennard-Jones potential. However, we must keep in mind that we need to fit only the relative energy values and not the gradients. The correct values of the gradients would be necessary when running the MD simulations, because the forces that are calculated during the run rely on the correct values of the gradients. However, in the case of the GCMC simulation, the acceptance/rejection is solely based on the energy value, which allows us to treat the obtained results less strictly. The fitted and reference curves for all of the 14 considered structures are shown in Fig. 3.

3.2. Model description

The zeolite model used in this study is the periodic cell of faujasite with the lattice constant $A = B = C$ equals to 17.5 Å and the angles $\alpha = \beta = \gamma$ equal to 60°. Geometry and location of the cluster in faujasite framework were taken from Ref. [18–23]. The tetrahedric iridium cluster is coordinated to the Si-> Al substituted site and is located in the 6-ring. The model is presented in Fig. 4.

3.3. Methods

The GCMC method (Grand Canonical Monte Carlo) [30] is an outstanding tool for the modeling of sorption in porous materials and is a type of simulation that concerns a system that has a constant chemical potential, volume and temperature. GCMC simulation is based on changes in the position and orientation of the molecules as well as the number of molecules in the system. According to this approach, three types of steps are allowed – insertion of a new molecule in a random configuration, removal of a molecule, and a change in a molecule's position/orientation. Every time, the move is checked if the new state comes with a lower energy with respect to the initial state and is being accepted or rejected. However, the new state with higher energy than the old one, however, could be accepted if the energy difference between the new and old states satisfies the acceptance criterion (Eq. (2)) [31]:

$$\min \left[1, \ \exp \left(\frac{E_0 - E_n}{KT} \right) \right] \tag{2}$$

Performing a simulation in which a series of Monte Carlo steps are being evaluated leads to thermodynamic equilibrium with respect to the chemical potential of the adsorbate, which in adsorption simulations corresponds to the adsorption equilibrium. Having the energy calculated for each step, it is possible to project it to the molecule's location/orientation and, in this way, generate a map of the mass distribution with respect to the interaction energy, which opens the possibility of identifying preferable/unpreferable adsorption sites.

In this study, we have performed the adsorption calculations in Sorption module of the Accelrys Materials Studio v. 6.1. In all simulations, number of equilibration steps was equal to 1 million and number of production steps to 10 million (what corresponds to "ultra-fine" settings). We have concluded, that these settings are sufficient to obtain trustful and high-quality mass distribution as increasing the number of steps does not bring changes in mass distribution. Cutoff distance value was equal to 18.5 Å and atom based summation method was selected for both Lennard-Jones and Coulomb potentials.

4. Results and discussion

The distribution of CO_2 molecules in the pores of the investigated system is shown in Fig. 5.

Each colored area represents the center of mass of the CO_2 molecule upon each accepted step of the GCMC scheme. The color
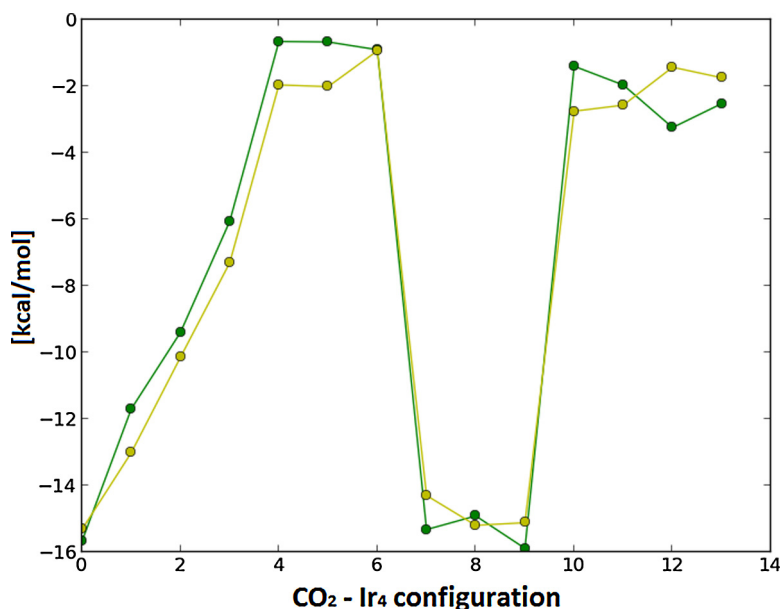

Fig. 3. Reference energy [kcal/mol] curve (yellow line) and the curve that results from fitting the parameters to the Lennard-Jones potential (green line) for all 14 geometries used for fitting. For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.
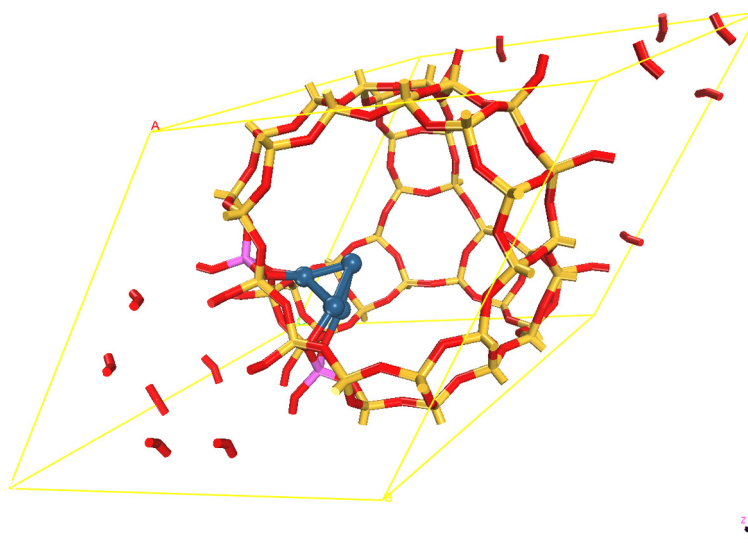
Fig. 4. Model of faujasite with the Ir_4 cluster used in the simulations.

represents the energy of interaction between the CO_2 molecule and the host system (zeolite + Ir_4 cluster): the blue, green and red colors represent the most stable, intermediate and weak interactions, respectively. The empty areas represent the volume where no adsorption takes place. There are characteristic green spots that are visible on the border of the cell. The cell border "cuts" the mass cloud and unveils the internal part of the cloud. The green internal part of the cloud is surrounded by the red outer part. This arrangement represents the optimal distance from the surface as determined by forcefield parameters.

Three types of clouds are immediately visible. The lowest energy locations are next to the Ir_4 cluster, where the interaction with the cluster is the main component. These areas are relatively well localized, which means that the adsorption in these sites is strong, and the molecule that is adsorbed there is allowed to move only, within a small distance. This molecules also block the neighboring sites for the other molecules, which can be seen in Fig. 5 as the empty area. It is possible to distinguish two types of sites: those on the edges of the cluster and those on top of it.

The largest mass cloud is also the most delocalized cloud. It represents the adsorption of the CO_2 molecules to the wall of the zeolite pore. There is no strict adsorption site in this case, but each individual zeolite atom contributes to the overall adsorption

energy, and the molecules are evenly distributed on the pore's surface. Simulations show that in this system, there are two types of adsorption – monolayer and multilayer. In the area of the Ir_4 cluster, the shape and energy profile of the cloud indicates monolayer adsorption, because the cloud is highly localized and the interaction energy does not create an oriented gradient. A completely different case is the adsorption within the zeolite porous system – the
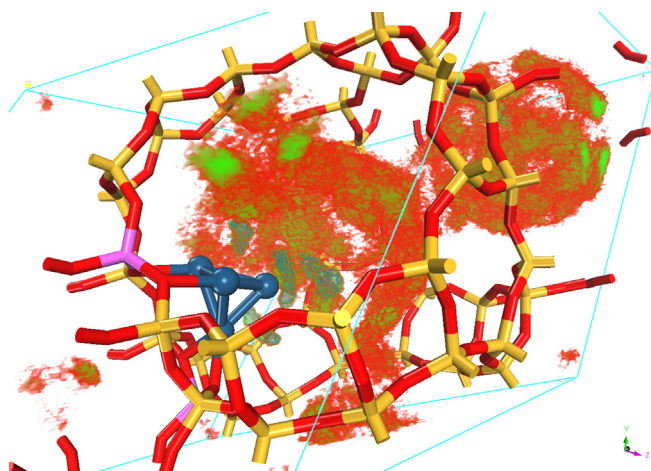

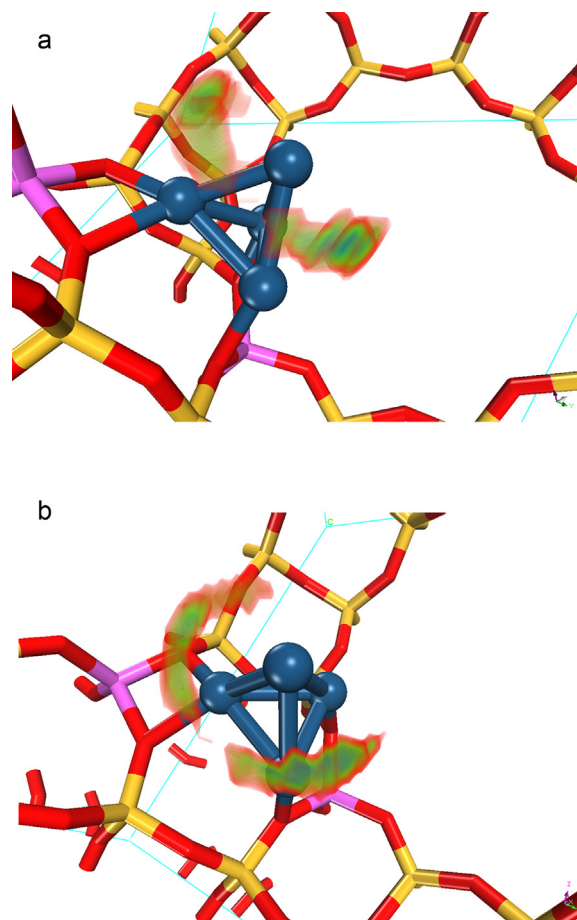**Fig. 5.** Distribution of the CO_2 molecules in the porous system of the investigated zeolite.

Fig. 6. Most preferable CO_2 adsorption sites in the porous system of Ir_4-supported Y zeolite, side view (a) and top view (b).
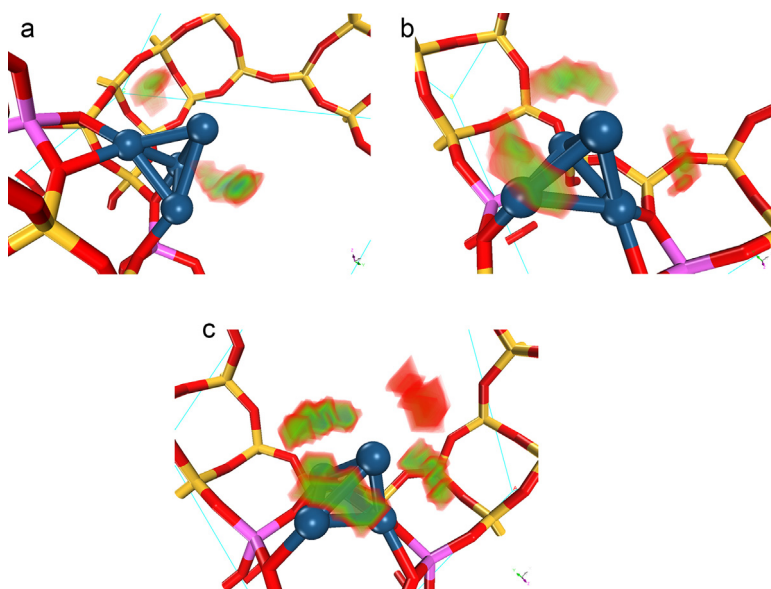
Fig. 7. Most preferable CO_2 adsorption sites in the porous system of Ir_4-supported Y zeolite. (a), (b) and (c) represent the fixed loading of 2, 3 and 4 CO_2 molecules, respectively.

mass cloud is delocalized through the accessible sites of the porous system and, in addition, the interaction energy shapes a gradient in which the strongest adsorption site is on the zeolite wall and the weakest is in the central area of the cage. According to those observations, it is possible to predict that the cluster adsorption site will be occupied in the first order, because it is accessible and provides the strongest interaction with the CO_2 molecule. While the cluster area gets saturated, CO_2 will start adsorbing on the zeolite walls instead of creating the next layers in the cluster area. The process of adsorption will continue by forming the next layers on the zeolite walls, until reaching the adsorption capacity.

Better insight into the most stable adsorption sites can be achieved with a fixed loading (1 molecule) canonical Monte Carlo simulation. This approach allowed us to identify the most preferable adsorption sites, which are located in the accessible area of the cluster, This arrangement is presented in Fig. 6a and b.

The result of this simulation is consistent with the previous simulation – the most favorable adsorption area is situated in the cluster's zone. It is noticeable that the location and shape of the

cloud is the cumulative effect of both the CO_2 – cluster and CO_2 – zeolite interactions. Theoretically, there is sufficient space to adsorb four molecules on the cluster, constituting three at the side and one at the top; however, one of the side locations is slightly less preferred than the other two locations, because of its closer distance to the zeolite wall.

The second type of site, which has a slightly weaker adsorption, is the adsorption on top of the Ir_4 cluster. This arrangement is consistent with the optimal geometry that is obtained from the DFT simulations. The interaction is weaker because it comes only from the Ir_4 cluster, and the zeolite wall is out of the interaction range. This area of adsorption is also strictly localized, which is similar to the first adsorption site described above. This arrangement is also consistent with the DFT-obtained geometries.

Interestingly, the location of the cluster in the 6-membered ring of the zeolite partially exposes two vertices of the Ir_4 tetrahedron to the empty volume of the pore. Theoretically, additional top sites could be occupied by CO_2 molecules; however, we have not observed this arrangement. The reason is that the optimal distance from the adsorption site is characteristic of the chemisorption, where the distance between the Ir and CO_2 molecule is smaller. This pattern would require a placement of the CO_2 molecule at a much shorter distance, where the repulsion from the zeolite framework prevails. Additionally, occupation of these additional top sites would be not necessarily a physical state. While the top corner Ir is bonded only to the Ir atoms, the 3 other Ir atoms are additionally bonded to the zeolite six ring; thus, with respect to the electronic structure, the top corner Ir is not equivalent to the other Ir atoms.

In general, the edge locations provide slightly stronger interactions than the top site because, at the top of the cluster, CO_2 interacts mainly with Ir_4, while at the side, it interacts with both Ir_4 and zeolite. It is apparent that the two edge locations provide the strongest (and equal) interactions, and the third edge location is affected (weakened) by the zeolite geometry.

As it has already been mentioned, for the isolated cluster, the most preferable configuration is the top corner site, and the edge locations appear to be less preferable. However, these relations might be distorted for a cluster that is embedded in the zeolite framework, where CO_2 interacts with both the cluster and zeolite.

Importantly, the order of the interactions is reversed. While the top sites are the most stable sites from the DFT simulations, the edge
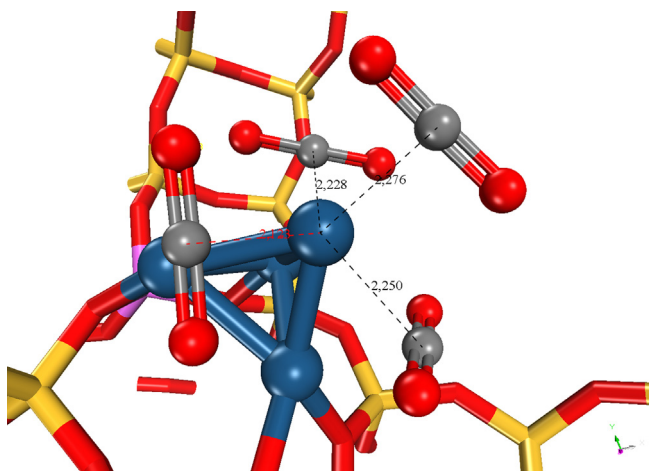

Fig. 8. Possible adsorption sites at the cluster. Three CO_2 molecules in the side location and one at the top.
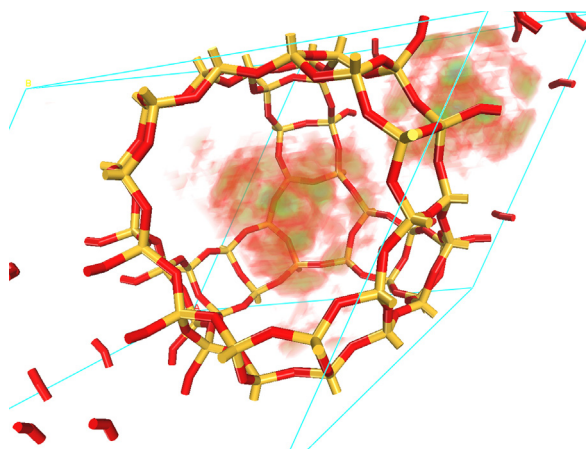
Fig. 9. Most preferable CO_2 adsorption sites in the porous system of pure silica Y zeolite.
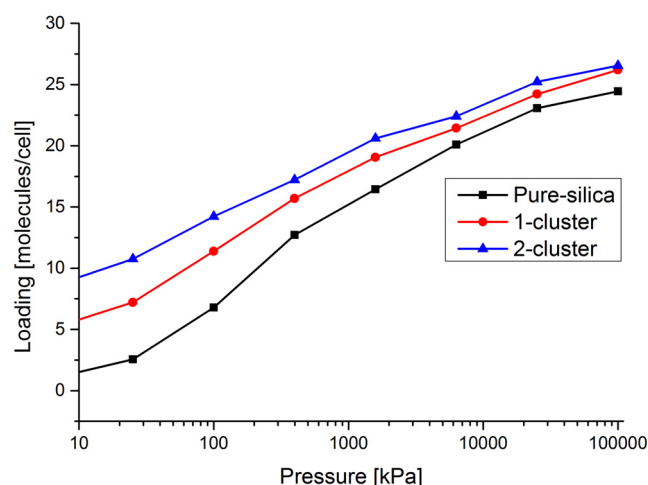

Fig. 10. Adsorption isotherm for the pure silica (black) and Ir_4 cluster-supported zeolite (single cluster – red, double cluster – blue). For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.

sites are more stable, as described by the forcefield. We attribute this effect to the presence of the zeolite framework, which is also the source of the interactions with CO_2 that are not accounted for in the fitting scheme. The zeolite framework interacts more strongly with a CO_2 molecule that is already immobilized by the Ir_4 cluster. We must note that these edge sites that were obtained from the FF simulations are similar in terms of geometry to the rotated transition state-like structures that were obtained from the DFT simulations. The height of the energy barrier calculated is 13.6 kcal/mol, which is close to the strengthening effect of the zeolite interaction and accounts for reversing the order of the interactions. Essentially, this part is the most artificial part of our fitting scheme, where the electronic effects of the interaction are too strong to be properly described with the simple Lennard-Jones potential. The total error introduced by this effect is, however, relatively small. The CO_2 positions on the edge sites are very close to the TS-like configurations that were obtained from DFT. Because the same site is occupied by the CO_2 molecule in both cases, it blocks the site from other molecules in the same way regardless of the orientation of the molecule, while maintaining comparable energy in both cases.

According to the simulations of adsorption of a single molecule, the cluster site is occupied in the first order. This finding agrees with the settlement of the molecules in a configuration that provides the strongest interactions between Ir_4 and zeolite. To verify this result, another set of simulations was performed, with fixed loading set to 2 and 3. Adsorption site maps are presented in Fig. 7.

Simulations with fixed loading confirm that the first CO_2 molecule will be adsorbed in one of the two more favorable side locations because the third side location is slightly less preferred due to the zeolite geometry. This third side location will be occupied by the third molecule. After occupation of all three side adsorption locations, the next molecule will settle at the top of the Ir_4 cluster Fig. 8.

A similar simulation, with a fixed loading of 1 molecule, was performed for pure silica Y zeolite. In this case, there is no strictly located adsorption site; the cloud is evenly distributed in the whole porous system and, in addition, a multilayer adsorption is visible (Fig. 7), which is similar to the third (delocalized) type of adsorption in the first simulation.

This arrangement means that, in pure silica faujasite, there is no specific, exactly defined, adsorption site. This result arises from the homogeneous structure of pure silica faujasite, which is composed only of SiO_4 tetrahedrons; this arrangement introduces equal contributions (tuned by the zeolite structure) to the CO_2 – zeolite interactions.

The introduction of Ir_4 clusters perturbs the mass cloud shape within the whole cage, while in the pure silica zeolite, the cloud forms a sphere that is slightly stretched in the direction of the channels; in Ir_4-supported zeolite, the mass cloud is definitely less regular and is shaped approximately as a half sphere with a hollow inside, where the chemisorption sites are located.

Interesting observations resulted from the calculation of adsorption isotherms for Ir-supported zeolite as well as for pure silica zeolite. In one zeolite cell, there are 4 six-rings in which an Ir_4 cluster can be introduced; thus, it is theoretically possible to construct models with 1, 2, 3 and 4 clusters in a zeolite cell. We have decided to exclude 3- and 4-cluster configurations because such high loading of the Ir is not physically plausible. This limitation has been confirmed by the DFT calculations: geometry optimization resulted in the deformation and disintegration of the clusters. We must keep in mind that a double cluster configuration might also not be necessarily physically plausible, but it allows us to observe the effect of doubling the interactions in an easy way.

Fig. 10 represents adsorption isotherms for the 298 K temperature for the Ir_4-supported zeolite (single and double cluster) and for the pure silica zeolite. It is visible on the isotherms that loading under the same pressure is always higher for the zeolite-supported Ir_4 cluster. This finding means that the introduction of a cluster to the zeolite enhances the adsorptive properties of the system by increasing the adsorption capacity. This effect is observable for single- and double-cluster models. Although the introduction of a cluster reduces the volume of the porous system, the cluster causes the adsorption process to intensify; thus, in total, the adsorption capacity is higher than for pure silica zeolite.

The difference in loading is especially visible under lower pressures (under 1000 kPa); thus, the cluster improves the adsorptive properties especially at the lower pressures. In this pressure range, the isotherm for a pure silica zeolite shapes a subtle hole, whereas the isoterm of the Ir-supported systems is more flat. This finding confirms that the adsorption properties of zeolite can be tuned by the incorporation of the Ir_4 clusters to the zeolite structure. In the context of carbon capture processes, it should be highlighted that the cluster enhances adsorption especially under lower pressures.

Under high pressures, the effect of interaction is less important, and the main role is played by the pressure only. This finding is very apparent when comparing isotherms for one- and two-cluster models: the difference in loading decreases with the increase in

pressure, and at the final point, the curves match. At high pressures, the adsorption is mainly of a physical nature, and depends almost only on the interactions between the CO_2 molecules present in the system. Additionally, the second cluster takes some part of the volume in the porous structure and enhances only the chemisorption process where the CO_2/surface interactions play a major role. For this reason, the difference in the loading decreases when the pressure rises.

5. Conclusions

In this work, we have combined parameters from the Garcia-Sanchez forcefield and parameters for the Ir cluster, which were fitted in our study, to investigate the adsorption properties of faujasite-supported Ir_4 clusters toward CO_2. Zeolite structures with one and two Ir_4 clusters per cell were accounted for. To indicate the influence of cluster introduction toward the adsorption process, pure silica faujasite was additionally included in the study.

It was found that a carbon dioxide molecule can be chemisorbed on the Ir_4 cluster with the adsorption energy of -15.3 kcal/mol (Fig. 1a). Additionally, a transition state between two chemisorbed states was discovered. The barrier of transfer from one top corner to another is 13.6 kcal/mol and is only slightly lower than the energy of desorption. It must be emphasized that this value concerns the interactions between the pure cluster and CO_2 (and not the zeolite-supported cluster).

GCMC simulations provide interesting observations on the adsorption process. Introduction of the cluster to the faujasite structure results in a significant change in the adsorption properties of this porous material. While in pure silica zeolite, the mass cloud is delocalized and evenly distributed in the whole porous system, and one type of adsorption is visible; in cluster-supported zeolite, two general types of adsorption processes are observable: strictly localized adsorption in the cluster zone (which corresponds to the chemisorption process) and the type of adsorption that is similar to in pure silica zeolite (which corresponds to physical adsorption). However, the mass cloud shape is distorted (Fig. 5 vs. Fig. 9) due to the presence of the cluster, which not only takes some volume in the porous system, but also interacts with CO_2 molecules differently. In consequence, the cluster area is reserved only for localized adsorption type (possible chemisorption) and this causes the distortion of physisorption mass cloud.

Because the CO_2 molecule interacts more strongly with the cluster than with the same zeolite, the cluster area is the most preferable adsorption site. Detailed examination of this process revealed that there are two types of adsorption sites around the cluster: at the top corner site and at the edge sites. In total, there is space for 4 CO_2 molecules – one at the top and three at the edges of the cluster, where the edge positions are slightly more preferable than the top site. The reason for this difference is that the adsorption of CO_2 is affected by both the CO_2 – cluster and CO_2 – zeolite interactions. Additionally, the cluster–zeolite interactions can also affect the cluster – CO_2 interactions.

Analysis of the adsorption isotherms brings information about the adsorption capacity of the investigated systems, which is increased by the introduction of Ir_4 clusters to the faujasite. Although the introduction of a cluster requires some volume in the porous system, the total result brings improvement in the adsorption capabilities. The greatest difference between the adsorption capacity of pure silica, single- and double-cluster structures is under 1000 kPa.

Chemisorption (and possible activation) of carbon dioxide makes faujasite-supported Ir_4 clusters an interesting candidate for carbon capture with possible further catalytic processing. While pure silica faujasite is able only to physisorb CO_2, faujasite with the Ir_4 cluster is able to chemisorb CO_2 on the cluster and, at the same time, is characterized by a higher adsorption capacity, especially under lower pressures. A chemisorbed and possibly activated CO_2 molecule might be a good starting point for a catalytic reaction.

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References

[1] M. Aresta, A. Dibenedetto, The contribution of the utilization option to reducing the CO_2 atmospheric loading: research needed to overcome existing barriers for a full exploitation of the potential of the CO_2 use, Catal. Today 98 (2004) 455–462.

[2] W. Wang, S. Wang, X. Ma, J. Gong, Recent advances in catalytic hydrogenation of carbon dioxide, Chem. Soc. Rev. 40 (2011) 3703–3727.

[3] A. Yamasaki, An overview of CO_2 mitigation options for global warming—emphasizing CO_2 sequestration options, J. Chem. Eng. Jpn. 36 (2003) 361–375.

[4] A.M. Ferrari, K.M. Neyman, M. Mayer, M. Staufer, B.C. Gates, Rosch, Faujasite-Supported Ir_4 Clusters: a density functional model study of Metal-Zeolite interactions, J. Phys. Chem. B 103 (1999) 5311–5319.

[5] J. Kim, L. Lin, J.A. Swisher, M. Haranczyk, B. Smit, Predicting large CO_2 adsorption in aluminosilicate zeolites for postcombustion carbon dioxide capture, J. Am. Chem. Society 134 (2012) 18940–18943.

[6] N.A.M. Razali, K.T. Lee, S. Bhatia, A.R. Mohamed, Heterogeneous catalysts for production of chemicals using carbon dioxide as raw material: a review, Renew. Sust. Energ. Rev. 16 (2002) 4951–4964.

[7] M.V.S. Sivaiaha Petit, J. Barraulta, C. Batiot-Dupeyrata, S. Valange, CO_2 reforming of CH_4 over Ni-containing phyllosilicates as catalyst precursors, Catal. Today 157 (2010) 397–403.

[8] M.C.J. Bradford, M.A. Vannice, CO_2 reforming of CH_4, Catal. Rev. 41 (1999) 1–42.

[9] H. Arakawa, J. Dubois, K. Sayama, Selective conversion of CO_2 to metanol by catalytic hydrogenation over promoted copper catalyst, Energ. Convers. Manage. 33 (1992) 521–528.

[10] H. Kusama, K. Okabe, K. Sayama, H. Arakawa, CO_2 hydrogenation to ethanol over promoted Rh/SiO_2 catalysts, Catal. Today 28 (1996) 261–266.

[11] T. Inui, T. Yamamoto, M. Inoue, H. Hara, T. Takeguchi, J. Kim, Highly effective synthesis of ethanol by CO_2 hydrogenation on well balanced multi-functional FT-type composite catalysts, Appl. Catal. A-Gen. 186 (1999) 395–406.

[12] Q. Zhang, Y. Zuo, M. Han, J. Wang, Y. Jin, F. Wei, Long carbon nanotubes inter-crossed Cu/Zn/Al/Zr catalyst for CO/CO_2 hydrogenation to methanol/dimethyl ether, Catalysis Today 150 (2010) 55–60.

[13] I.A. Fisher, A.T. Bell, A comparative study of CO and CO_2 hydrogenation over Rh/SiO_2, J. Catal. 162 (1996) 54–65.

[14] T.J. Lee, B.C. Gates, Rhodium in basic zeolite Y: a stable, selective catalyst for CO hydrogenation, J. Mol. Catal. 71 (1992) 335–346.

[15] G. Peng, S.J. Sibener, G.C. Schatz, M. Mavrikakis, CO_2 hydrogenation to formic acid on Ni(110), Surf. Sci. 606 (2012) 1050–1055.

[16] B. Chan, L. Radom, Design of effective zeolite catalysts for the complete hydrogenation of CO_2, J. Am. Chem. Soc. 128 (2006) 5322–5323.

[17] A.B. Laursen, K.T. Hojholt, L.F. Lundegaard, S.B. Simonsen, S. Helveg, F. Schuth, M. Paul, J.D. Grunwaldt, S. Kegnas, Christensen, K. Egeblad, Substrate size-selective catalysis with zeolite-encapsulated gold nanoparticles, Angew. Chem. Int. Ed. 49 (2010) 3504–3507.

[18] E.A. Ivanova Shor, V.A. Nasluzov, A.M. Shor, G.N. Vayssilov, Rosch, Reverse hydrogen spillover onto zeolite-supported metal clusters: an embedded cluster density functional study of models M6 (M=Rh, Ir, or Au), J. Phys. Chem. C 111 (2007) 12340–12351.

[19] G.P. Petrova, G.N. Vayssilov, Rosch, Density functional modeling of reverse hydrogen spillover on zeolite-supported tetrairidium clusters, Chem. Phys. Lett. 444 (2007) 215–219.

[20] B.C. Gates, Oxide- and zeolite-supported "molecular" metal clusters: synthesis, structure, bonding, and catalytic properties, Top. Organomet. Chem. 16 (2005) 211–231.

[21] A. Kulkarni, R.J. Lobo-Lapidus, B.C. Gates, Metal clusters on supports: synthesis, structure, reactivity, and catalytic properties, Chem. Commun. 46 (2010) 5997–6015.

[22] A. Uzun, D.A. Dixon, B.C. Gates, Prototype supported metal cluster catalysts: Ir_4 and Ir_6, ChemCatChem 3 (2011) 95–107.

[23] W.A.A. Weber Zhao, B.C. Gates, NaY zeolite-supported rhodium and iridium cluster catalysts: characterization by X-ray absorption spectroscopy during propene hydrogenation catalysis, J. Catal. 182 (1999) 13–29.

[24] G.P. Petrova, G.N. Vayssilov, Rosch, Density functional study of hydrogen adsorption on tetrairidium supported on hydroxylated and dehydroxylated zeolite surfaces, J. Phys. Chem. C 111 (2007) 14484–14492.

[25] B. Liu, B. Smit, F. Rey, Valencia, S.S. Calero, A new united atom force field for adsorption of alkenes in zeolites, J. Phys. Chem. C 112 (2008) 2492–2498.

[26] A. Garcia-Sanchez, C.O. Ania, J.B. Parra, D. Dubbeldam, T.J.H. Vlugt, R. Krishna, Calero, Transferable force field for carbon dioxide adsorption in zeolites, J. Phys. Chem. C 113 (2009) 8814–8820.

[27] S.L. Mayo, B.D. Olafson, W.A. Goddard, DREIDING: a generic force field for molecular simulations, J. Phys. Chem. 94 (1990) 8897–8909.

[28] O.S. Trushin, M. Kotrla, F. Maca, Energy barriers on stepped Ir/Ir(111) surfaces: a molecular statics calculation, Surf. Sci. 389 (1997) 55–65.

[29] P.M. Agrawal, B.M. Rice, D.L. Thompson, Predicting trends in rate parameters for self-diffusion on FCC metal surfaces, Surf. Sci. 515 (2002) 21–35.

[30] D. Frenkel, B. Smit, Understanding molecular simulation, From Algorythms to Application, second ed., Academic Press, 2002.

[31] Y. Zeng, S. Ju, W. Xing, C. Chen, Computer simulation of benzene adsorbed in all-silica Y and NaY zeolites, Ind. Eng. Chem. Res. 46 (2007) 242–248.