The role of Ir$_4$ cluster in enhancing the adsorption of CO$_2$ on selected zeolites – GCMC simulations

Daniel Smykowski [a],*, Kacper Nowak [a], Rafał Łużny [a], Jerzy Szczygieł [a],
Bartłomiej M. Szyja [b],[c],**

[a] Wrocław University of Technology, Department of Chemistry, Gdańska 7/9, 50-344 Wrocław, Poland
[b] Institute for Solid State Theory, Westfälische Wilhelms-Universität Münster, Wilhelm Klemm Str. 10, 48148 Münster, Germany
[c] Inorganic Materials Chemistry, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Den Dolech 2,
5612 AZ Eindhoven, The Netherlands

ABSTRACT

We have investigated the adsorption of CO$_2$ molecules inside the EMT, SAO, SBS, SBT and IWS zeolites with respect to the influence of the Ir$_4$ clusters on the adsorption capabilities of these materials. We have determined that the capabilities of CO$_2$ adsorption depend on the combined effect of the framework topology and the position of the Ir$_4$ cluster. Adsorption intensifies despite the fact that a fraction of the pore volume is occupied by the Ir$_4$ cluster, and thus, the adsorption is more intense than that on empty zeolite. The pore topology however is also playing a crucial role in the effect, as in certain cases it allows the CO$_2$ molecules to order in such a way they fill the most pore space.

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1. Introduction

The greenhouse gases emission is currently one of the most important issues standing in a way to a sustainable environment. Presently, carbon-based energy sources dominate radically over other sources, and it is predicted that this trend will stay unchanged [1,2]. The technology available currently, allows to reduce only a small fraction of very large carbon dioxide emission [3]. From this perspective, development of novel technologies to reduce the amount of CO$_2$ is a particularly important target. This process is referred to as carbon utilization [4] and can be done by several methods, with two most significant options emerging: storage and conversion [3].

The approach that is the most interesting from both academic and industrial point of view, is the chemical conversion of the CO$_2$ into valuable chemicals or energy carriers [5]. However, due to high thermodynamical stability of the CO$_2$ molecule, highly active catalysts to be developed [1,2,6]. This is challenging and costly task and makes the chemical processing of carbon dioxide is very difficult.

The methods of the CO$_2$ capture and storage seem to become available sooner and at lower cost. These methods rely on strong

interaction of the CO$_2$ molecules with the material, and for the solid sorbents it usually requires the highly developed porous surface of the material. Interestingly, the mechanism responsible for this process is important not only for the adsorbent design. As the adsorption is an essential step in the heterogeneous catalysis, and usually determines the overall performance of a catalyst [7] – enhanced adsorption ability can also lead to the development of the catalysts for the chemical conversion of CO$_2$. Thus, materials characterized by excellent adsorptive properties, which may be relatively easily modified to gain catalytic properties are at highest demand. A material, which is applicable for carbon capture today and can be modified and used for carbon dioxide conversion in the future is a special target of research.

Several materials have been proposed for the carbon dioxide capture. Metal organic frameworks [8] can be easily tailored to a specific application, and the presence of the unsaturated metal sites can play an important role. On the other hand, the CO$_2$ capture in the porous carbons relies mostly on the presence of the narrow micropores and not on any particular sites [9,10]. Zeolites occupy a particularly important space on the list of the carbon capture materials. Due to their selectivity, relatively low cost, ease of obtaining and high adsorption capacity, zeolites are considered as one of the most promising material groups. Their acid/base properties can be adjusted by changing the Si/Al ratio in the framework, or by the introduction of extra-framework species, like metal cations [11] or clusters [12] which can influence adsorptive properties. Zeolites with the acidic sites [13] are relatively easiest to apply in the

* Corresponding author. Tel.: +48 71 320 64 06.
** Corresponding author at: Wrocław University of Technology, Department of Chemistry, Gdańska 7/9, 50-344 Wrocław, Poland.
E-mail addresses: daniel.smykowski@pwr.edu.pl (D. Smykowski),
b.m.szyja@tue.nl (B.M. Szyja).

carbon capture process, due to the abundance of available commercial zeolites.

In the study of Pham et al. [14] the adsorption of N_2 and CO_2 on CHA, STT, BEA, MFI and FER zeolites was investigated computationally and experimentally. The authors found that interaction of zeolite with CO_2 is stronger than with N_2, which makes zeolites an attractive material group also for selective adsorption or gas separation.

Kim et al. [15] have taken the challenge to perform an extensive study of many zeolite structures and MOFs with respect to their CO_2-capture capabilities. The authors presented a list of 20 zeolites that outperform the rest of investigated structures in carbon-capture applications. Little details on the mechanism of the CO_2 adsorption on these zeolites have been provided though.

Keeping in mind that the hydrogenation of carbon dioxide is a redox reaction, metal-containing zeolites are also potentially good candidates for catalysts [16]. The metal clusters supported on zeolites exhibit an ability of hydrogen spillover and have been proposed by Rösch [17,18] to be the reducing agent for the hydrogenation. This feature of metal clusters, together with the variety of metal types and cluster sizes supported by zeolite frameworks of many possible pore topologies, opens wide possibilities of tuning of the catalytic properties. In the paper by Lee [19] it was confirmed experimentally that faujasite supported rhodium clusters are active in the hydrogenation of carbon monoxide to hydrocarbons. They exhibit higher stability and higher yields of C_2–C_5 hydrocarbons with respect to Rh/γ-Al_2O_3. This is determined by strong basicity of zeolite support as well as its porous structure.

An extensive investigation of structural and catalytic properties of zeolite supported metal clusters has been published by the group of B.C. Gates [20–22]. Their studies [23] bring insight into a catalytic activity of supported metal clusters and it was revealed that metal clusters bonded to oxide or zeolite supports, may combine advantages of solid catalysts with the selectivity of soluble molecular catalysts. This is, therefore, a promising route for designing novel, active and selective catalytic systems.

Our previous study [24] revealed similar effect of the metal/support interactions on the adsorption of CO_2. The introduction of iridium cluster in the faujasite structure is responsible for the increase the adsorption capacity due to the ability of the Ir_4 cluster to strongly interact and activate CO_2.

Structurally, tetrairidium clusters have been found to be coordinated with zeolite six rings [20–22], which are present not only in faujasite framework, but also in many other frameworks and may form various kinds of structural units like channels or cages.

2. Aim and scope of the study

This paper is the second one in the series and represents the incremental advance of our simulation work aimed to explain the mechanism of the enhancement of CO_2 adsorption caused by small metal clusters in zeolites. In the first paper [24] we have aimed to explain the interactions between the Ir_4 cluster and CO_2 molecule, in this work we extended the analysis to the possible influence of the zeolite topology. It has to be stressed out, that the aim of this work was not the systematic analysis of many possible zeolite frameworks, but rather to explain the role of the zeolite framework and somewhat counter-intuitive volume exclusion phenomenon.

As finding the best candidate for a perfect sorbent is not the same as understanding the underlying mechanism of the CO_2 adsorption, we have decided not to carry out the systematic search, but rather focused on a bottom-up approach on a well described system of Ir_4 cluster bound to the zeolite 6-ring, and the effect of the framework has been fully taken into account by means of few model systems containing 6-membered rings.

Thus, the aim of this work was to determine the mechanism of the Ir_4 clusters ability to enhance the adsorption properties of the given zeolite reported previously by Moon et al. [25], who suggest the CO_2 adsorption can be improved by the immobilization of the guest molecules inside the zeolite pores. This in turn allows to align the guest molecules tighter together in contrast to their disordered distribution.

We expect that this ordering will only be favored in the particular channels – especially the channel dimensions and the position of the cluster in the pores will play an important role. We expect that the pore diameter limitations would start playing an important role especially in the narrow pores, where the cluster takes already significant space. Therefore, we have chosen a few different zeolite frameworks for the investigation, based on their differences in the porous structure.

The selection of these particular structures was not so straightforward. The extensive screening of the zeolite structures has been performed in the group of Kim et al. [15]. A set of 20 of analyzed zeolite frameworks performed particularly well in the adsorption of carbon dioxide, however due to the nature of their analysis, no conclusions on the adsorption sites can be drawn, because it is simply not possible to describe in details the adsorption process for each of such an extensive set of structures.

For the needs of the current work, we have selected a set of few structures of the best performing ones. The additional criterion was the presence of six-rings in the zeolite framework as according to Rösch et al. [20–22] these structures are able to support Ir_4 clusters and according to the best of our knowledge there is no atomic level details available for other type of Ir/zeolite geometries. It has to be emphasized, that the faujasite, which belongs to this class as well, has been investigated in the study presented in our previous paper in this series [24].

3. Model and computational details

This work is an incremental advance of the Ir_4/zeolite studies done in our group, that has been published previously [24]. For the sake of completeness, only the crucial set of parameters and description is repeated here. For the additional discussion and computational details, the reader is referred to the first paper.

The Grand Canonical Monte Carlo (GCMC) method is perhaps the best suited tool to provide us with all details of the adsorption process interesting in this study. This method has been successfully used for these purposes for decades and it is proven to provide trustworthy results [15]. However, as it is the case in all types of simulations, the quality of the results can only be as good as the model used. In particular, the quality of the simulation of sorption depends greatly on the potential describing interatomic interactions.

Among numerous forcefields parametrized for adsorption simulations, a new forcefield is available [26] that has been developed to describe the CO_2/zeolite systems. The authors aimed to provide good agreement with the experimental adsorption isotherms and optimize the speed of calculations. In practice, this allows to simulate the systems, which require large number of GCMC steps to converge and reach thermodynamic equilibrium.

The Ir parameters are not a part of the original forcefield, and have been fitted by us previously, based on the DFT simulations [24]. Admittedly, these parameters are intentionally only suitable for tetrairidium clusters, and enabling transferability to clusters of different geometry and sizes is still under development in our group.

While the atomic charges for Si, Al and O (zeolite) are included in the original forcefield, the charges of the iridium atoms are not present in the paper. However, the charges calculated with the

Table 1
The complete list of the forcefield parameters used in this study. Parameters in italic have been fitted within our study [24], the other ones have been taken from Garcia-Sanchez forcefield [26].

Atom type	Atomic charge	Atom pair	D_0 [kcal/mol]	R_0 [Å]
q(O)CO2	−0.32560	O_{CO_2}–O_{CO_2}	0.0426	3.3865
q(C)CO2	0.65120	C_{CO_2}–C_{CO_2}	0.0149	3.0812
q(Si)	0.78598	O_{CO_2}–C_{CO_2}	0.0252	3.2327
q(Al)	0.48598	O_{CO_2}–O_{zeo}	0.0392	3.6334
q(O)zeoSi	−0.39299	C_{CO_2}–O_{zeo}	0.0187	3.9410
q(O)zeoAl	−0.41384	Ir–O_{CO_2}	*0.0368*	*3.0289*
q(Ir)	*0.103–0.292*	Ir–C_{CO_2}	*0.0218*	*2.8891*

Hirschfeld method for the zeolite atoms, multiplied by a coefficient equal to 1.5 match those of the Garcia-Sanchez forcefield very well. Therefore, this method has been used to assign charges for both zeolite atoms and for the Ir cluster to preserve consistency in the electrostatic effects in the system. Only for the CO_2 molecule the atomic charges were gathered directly from the article. The values of atomic charges included in the Garcia-Sanchez forcefield are presented in Table 1.

The forcefield has been implemented in Accelrys Materials Studio 6.1, to allow it to use with the Sorption module.

3.1. Model description

The zeolite models used in this study are the periodic cells taken from Accelrys Materials Studio V6.1 structure database [27] and the Database of Zeolite Structures provided by International Zeolite Association [28]. Five zeolite structures, SAO [29], EMT [30], SBS [31], SBT [31] and IWS [32] has been used in our simulations. Structural parameters (lattice constants and angles) are presented in Table 2.

Tetrairidium clusters in the faujasite have been found to coordinate to the 6-membered ring with Si→Al substitution [17,18,20–22,33]. We have kept this configuration, including only the two Si→Al substitutions in the 6-membered ring. In order to avoid the complications in analysis caused by Brønsted acid sites of extra-framework cations, we have decided to keep other Si atom unsubstituted. The exact geometry of the cluster has been adopted from the Refs. [17,18,20–22]. We have assumed that the position of the Ir_4 cluster relative to the zeolite 6-ring is always the same, and the zeolite topology has no influence on it. As the six-rings present in investigated zeolite structures do not differ substantially in terms of geometry, we decided not to perform any additional geometry optimizations.

There are multiple six-rings in the framework of each of selected zeolites, however it has to be pointed out, that due to the symmetry of the zeolite frameworks, only few of these 6-rings are unique. In addition, all 6-ring structures are very similar and the interaction energy of the Ir_4 cluster with the zeolite is for that reason also very similar. As the amount of the calculations necessary to plot the adsorption isotherms in all possible combinations available to support the iridium clusters is not feasible, we have decided to arbitrarily select the most representative locations of the Ir_4 clusters. In the selection of these systems we have taken into account avoiding duplication of structures by rejecting symmetry copies and only one cluster can be present in each zeolite cage. Symmetry

identical copies do not bring any value to the analysis of the CO_2 mass distribution inside the zeolite pores and higher Ir content has to be treated with caution because already one Ir_4 cluster in faujasite unit cell corresponds to 21 wt%. Structure and location of Ir_4 clusters in each framework is presented in Fig. 1.

The important point is the activation of CO_2 molecule on the Ir_4 cluster. This mechanism we have also exploited in our previous study [24] with the conclusion that the immobilization of the activated CO_2 molecule(s) at the cluster is responsible for the increase of the number of adsorbed molecules. We have found that the straight/bent conformations of the CO_2 molecule do not play an important role here due to the fitting of the forcefield parameters for the Ir–C and Ir–O pairs that already compensated for the conformational changes.

3.2. Methods

The Grand Canonical Monte Carlo [34] is a stochastic method that simulates a system having a constant volume V (the pore with the adsorbed phase), in equilibrium with an infinite reservoir of particles imposing its chemical potential μ and temperature T [34,35]. Use of the grand canonical ensemble allows to estimate the number of molecules adsorbed in the system [36]. Execution of a simulation in which a series of Monte Carlo steps are being evaluated, results, in the case of adsorption simulations, with the adsorption equilibrium.

In a GCMC simulation, three types of actions are allowed – insertion of a new molecule in a random configuration, removal of an existing molecule, and a change in a molecule's position/orientation. After every action, the energy of the system is evaluated and compared to the energy of the preceding state. In terms of the energy, the new state is being accepted if the condition given by Eq. (1) is fulfilled [37]

$$p_{move} = \min \left[\exp \left(\left(\frac{\Delta U}{kT} \right) \right) ; 1 \right] \tag{1}$$

where ΔU ($U_{new} - U_{old}$) is the difference in energy of initial state the energy of considered state. The probability of acceptance of insertion (p_{ins}) and deletion (p_{del}) is expressed with Eqs. (2a) and (2b) respectively:

$$p_{ins} = \min \left[\frac{V}{N+1} \exp \left(\frac{\mu - \Delta U}{kT} \right) ; 1 \right] \tag{2a}$$

$$p_{ins} = \min \left[\frac{N}{V} \exp \left(\frac{\Delta U - \mu}{kT} \right) ; 1 \right] \tag{2b}$$

Table 2
Structural parameters of zeolite cells used in the study.

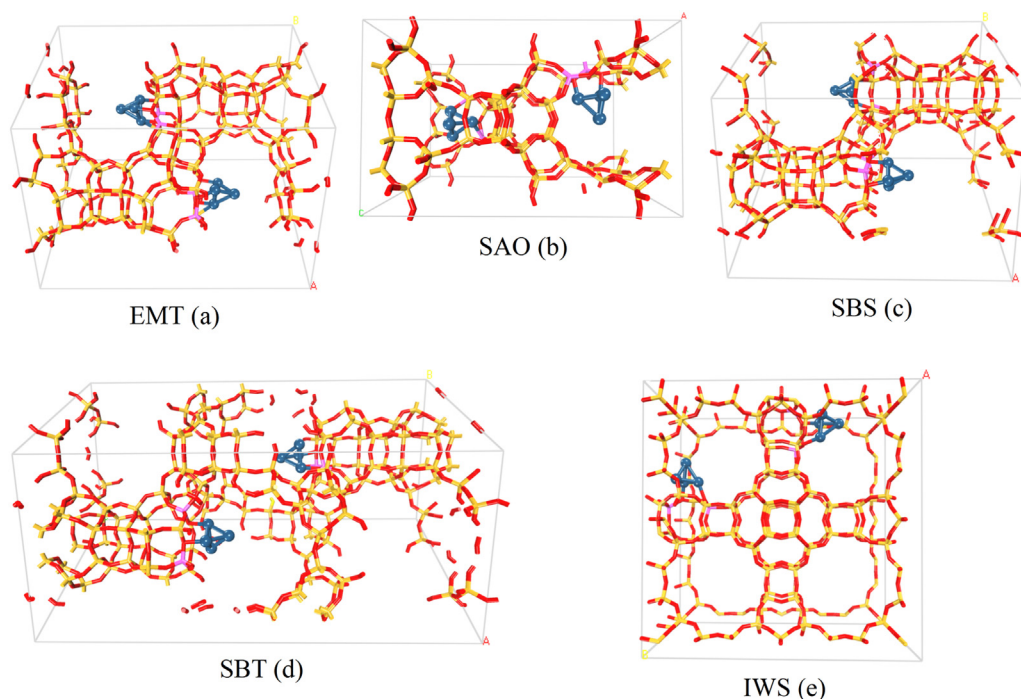| Zeolite	Lattice constants [Å]	Angles [°]	Number of 6-rings (unique)
SAO	$A = B = 13.439$; $C = 21.860$	$\alpha = \beta = \gamma = 90°$	8 (2)
EMT	$A = B = 17.449$; $C = 28.455$	$\alpha = \beta = 90°$; $\gamma = 120°$	20 (2)
SBS	$A = B = 17.193$; $C = 27.333$	$\alpha = \beta = 90°$; $\gamma = 120°$	16 (2)
SBT	$A = B = 17.191$; $C = 41.030$	$\alpha = \beta = 90°$; $\gamma = 120°$	14 (2)
IWS	$A = B = 26.689$; $C = 12.908$	$\alpha = \beta = \gamma = 90°$	28 (3)

Fig. 1. (a–e) Models of zeolites with the Ir$_4$ cluster used in the simulations.

where V stands for volume, T for temperature, N for the number of adsorbate molecules and μ for chemical potential.

An useful technique is to correlate the energy for each step with the location of the molecule inside the pores. This results in a map of the mass distribution with respect to the interaction energy, which finally allows to indicate preferable/unpreferable adsorption sites.

All adsorption calculations have been carried out 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 40 million. These settings were necessary to ensure the system converged to the thermodynamic equilibrium state. Thus, it allowed us to obtain trustworthy mass distribution as well as high-quality isotherms. The value of the cutoff distance was set to 18.5 Å and direct summation of the relevant potentials for each atom pair was applied for both Lennard–Jones and Coulomb terms. Adsorption isotherms were calculated for 298 K and for the pressure range 10–100,000 kPa in 10 fugacity steps. We have decided to present the mass cloud for an intermediate pressure of 1000 kPa as the most representative result. In low pressure the adsorption is dominated by chemisorption on the cluster and other locations of CO$_2$ inside the pores are not visible, whereas high pressure leads to the occupation of all available space and the preference with respect to the sites is not clearly seen from the CO$_2$ distribution. The arbitrary choice of 1000 kPa is therefore justified, as it allowed us to observe the distribution of the CO$_2$ under the influence of both types of sites.

4. Results and discussion

4.1. The distribution of adsorbed molecules in the pores

Fig. 2 represents the distribution of carbon dioxide molecules in the porous structure of EMT zeolite. Every point in the visible area represents the center of mass of the CO$_2$ molecule for each accepted GCMC step. In addition the points are colored according to the strength of interaction between the CO$_2$ molecule and the host system: the blue, green and red colors represent the most stable, intermediate and weak interactions, respectively (Fig. 2). The blank

spaces are the areas in the porous structure where adsorption has not occurred during the simulation.

The results obtained in current simulations are generally consistent with the ones for Ir$_4$-faujasite, published by us recently [24]. However, few significant differences for the investigated frameworks can be observed.

In general, in pure zeolite two types of areas in the whole mass cloud can be distinguished – the delocalized one in the central part is colored red, and the more localized spots directly on the zeolite walls are colored green. The second type is observed for most of the investigated systems and the areas of adsorption are separated from each other by an empty space. Each area represents the location of a single CO$_2$ molecule. The outer area of these clouds is usually of the red color, and represents the states, where a slight displacement of the CO$_2$ molecule from the optimal location causes the increase of the energy of the state.

Analogously to multilayer adsorption phenomenon, such as identified by Crabtree et al. [38] on faujasite, upon filling up all available adsorption centers of this type, CO$_2$ molecules start to occupy the central space of the pores, which is visible as red, delocalized areas of the mass cloud. In this case, the interaction with the zeolite walls is screened by already adsorbed CO$_2$ molecules, and therefore it is much weaker. These molecules are much more mobile, and do not occupy any particular space/position in the zeolite pore.

Another, significantly different type of adsorption can be observed on Ir$_4$-containing zeolite. In the area of the cluster, two adsorption types described above are excluded as the third type of adsorption (blue and greenish-blue cloud) dominates due to strong interaction between CO$_2$ and iridium cluster. This is also visible on the histogram in the form of a double peak at −45 and −40 kcal/mol. Unlike previous adsorption types, the mass cloud is strictly localized, what indicates that CO$_2$ molecules are being adsorbed in the very specific adsorption sites and their mobility is very limited.

Detailed insight into adsorption at the Ir$_4$ clusters reveals two types of adsorption sites: edge sites and top (vertex) sites. Remarkably, adsorption at the edge sites is stronger than on the vertex. The reason for this difference is that CO$_2$ molecule adsorbed at the
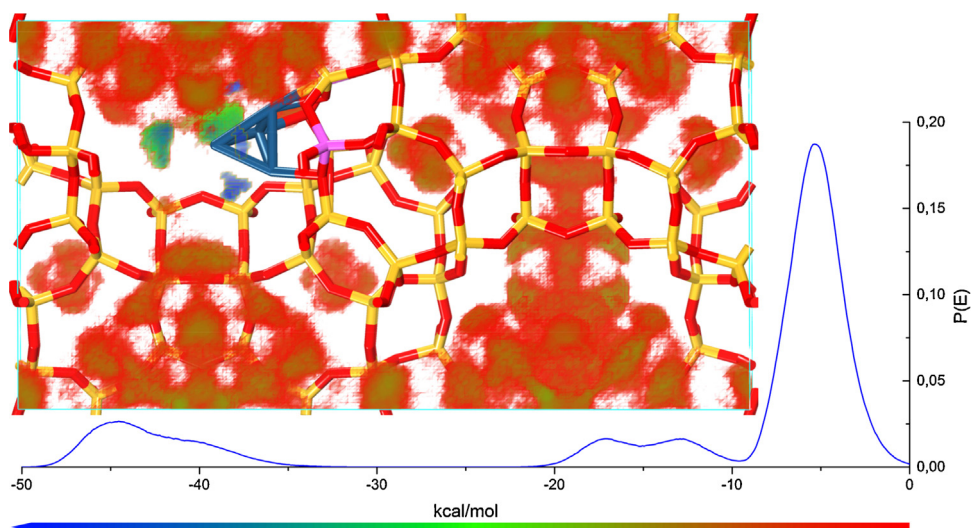
Fig. 2. Distribution of the CO_2 molecules in the porous system of EMT zeolite with one Ir_4 cluster and histogram of interaction energy [kcal/mol] in 1000 kPa.

edge sites interacts not only with the iridium cluster, but also with the zeolite as well, while at the vertex, the interaction with iridium dominates over faded interaction with zeolite. The location of the mass clouds representing the cluster adsorption sites is consistent for all studied frameworks, adsorbed CO_2 molecules are not likely to display radical differences in terms of adsorption modes. Different zeolite frameworks, which surround the six-ring and the cluster result with slight variations in interaction energy, however do not seem to perturb totally the geometry of adsorbed CO_2 molecules.

The framework structure of EMT zeolite that surrounds the six-ring allows one of the Ir_4 vertices to be exposed, which in turn enables this adsorption site to be occupied. This is a nice example of the indirect role of the zeolite framework in the enhancement of the adsorption properties.

As the strongest adsorption takes place in the area of the cluster, these adsorption sites are the most preferable ones, and during adsorption process, they will be occupied in the first order. Localized character of adsorption at the cluster allows to predict that

after saturation of cluster adsorption sites, next molecules will be contributing to a physical adsorption process, outside of the cluster area.

The same adsorption pattern is preserved in the case of pure silica SAO zeolite that is shown in Fig. 3. The overall shape of the mass cloud is determined by the porous system and multilayer adsorption is visible similarly to previous model.

Adsorption on Ir_4-SAO unveils, however, another significant effect. While the presence of the cluster in faujasite, EMT or SBS (Fig. 4) causes heavy distortion of the mass cloud in its area, in SAO zeolite this effect is minor, because the cluster occupies the space that remains mostly unoccupied by CO_2 molecules in pure zeolite. It means that the cluster position plays a crucial role – it can be placed in the space originally covered by a significant part of the cloud (as for EMT or faujasite) or in the area does not importantly contribute in physical adsorption (as for SAO). In the first case, the cluster affects the physical adsorption substantially, while in the second case its influence on physisorption is minor. It can be expected,
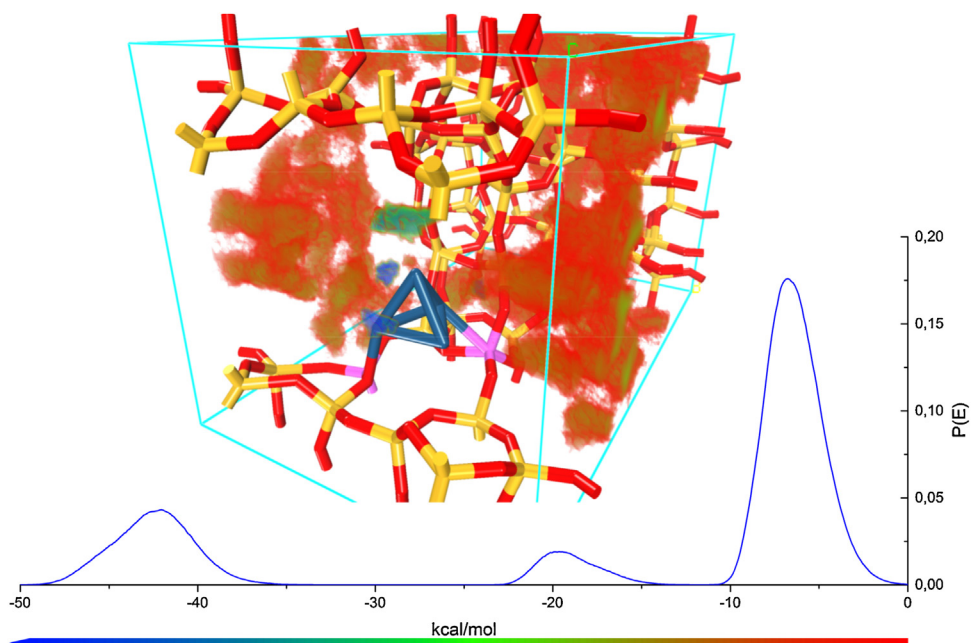

Fig. 3. Distribution of the CO_2 molecules in the porous system of SAO zeolite with one Ir_4 cluster and histogram of interaction energy [kcal/mol] in 1000 kPa.
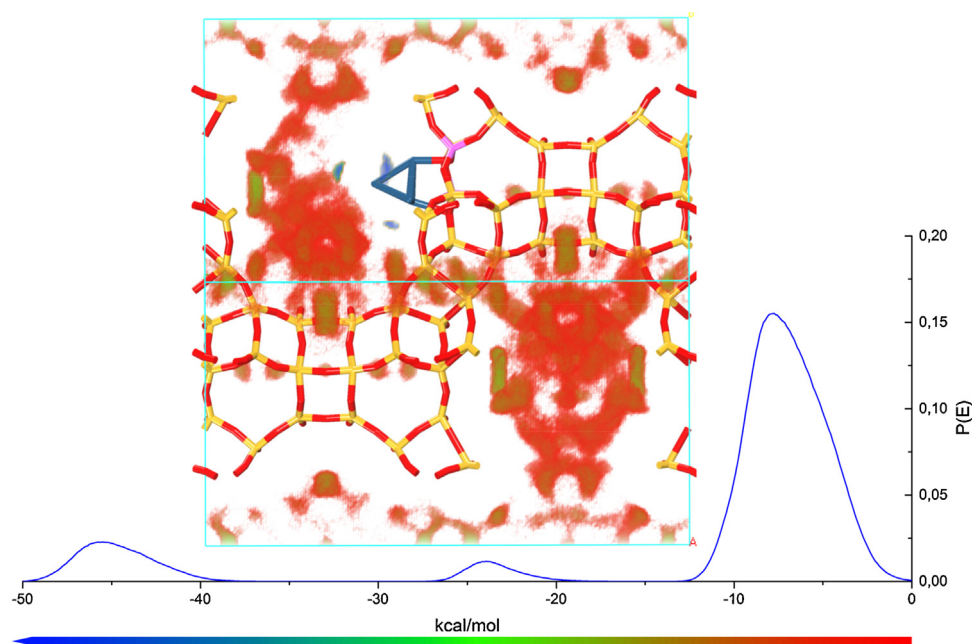
Fig. 4. Distribution of the CO_2 molecules in the porous system of SBS zeolite with one Ir_4 cluster (a) and representation of adsorption sites at the Ir_4 cluster (b).

that this dependence will have direct consequence in the number of adsorbed molecules at different pressures and will determine the shape of isotherms.

With respect to this effect, SBT (Fig. 5) and IWS (Fig. 6) zeolites are an intermediate cases, between EMT, in which the cluster distorts the mass distribution significantly and SAO, in which the distortion is minor. The Ir_4 cluster inserted in the framework of SBT or IWS, changes the shape of mass cloud only partially. This observation is further supported by the analysis of the adsorption isotherms.

4.2. Adsorption isotherms

Analysis of adsorption isotherms allowed us to characterize adsorption capacity of investigated systems and indicate the influence of the cluster in the whole pressure range. Similarly to our previous study [24], we have found that for the most of investigated zeolites, the Ir_4 cluster increases the adsorption capacity of

pure-silica faujasite in low pressure range (<1000 kPa) and the difference in adsorption capacity decreases with the increase of the pressure. This is intuitive, as in low pressure range the number of guest molecules is low, and the presence of Ir cluster enables the sites of the strong adsorption, that are not present otherwise. The increased pressure causes more molecules to adsorb, and occupy all available volume of the pores, and this is where the space occupied by the Ir_4 cluster comes into play. The number of CO_2 molecules as compared to the pure zeolite cannot increase any further.

This is, however, not the case for the SAO zeolite, as the number of adsorbed molecules still increases despite the fact the cluster occupies some of the volume in the pore. We conclude that the strongly adsorbed CO_2 molecules are immobilized in particular positions by the interactions with the Ir_4 clusters, and this in turn allows other CO_2 molecules to fit better in the space still available in the pores. This suggests the effect of capillary condensation, but basing on the obtained results we cannot conclude this definitively.
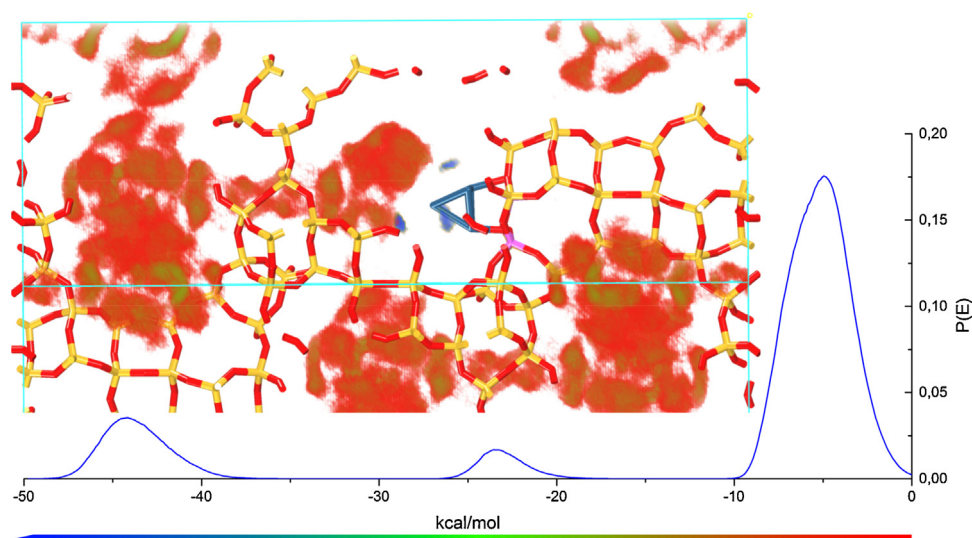

Fig. 5. Distribution of the CO_2 molecules in the porous system of SBT zeolite with one Ir_4 cluster (a) and representation of adsorption sites at the Ir_4 cluster (b).
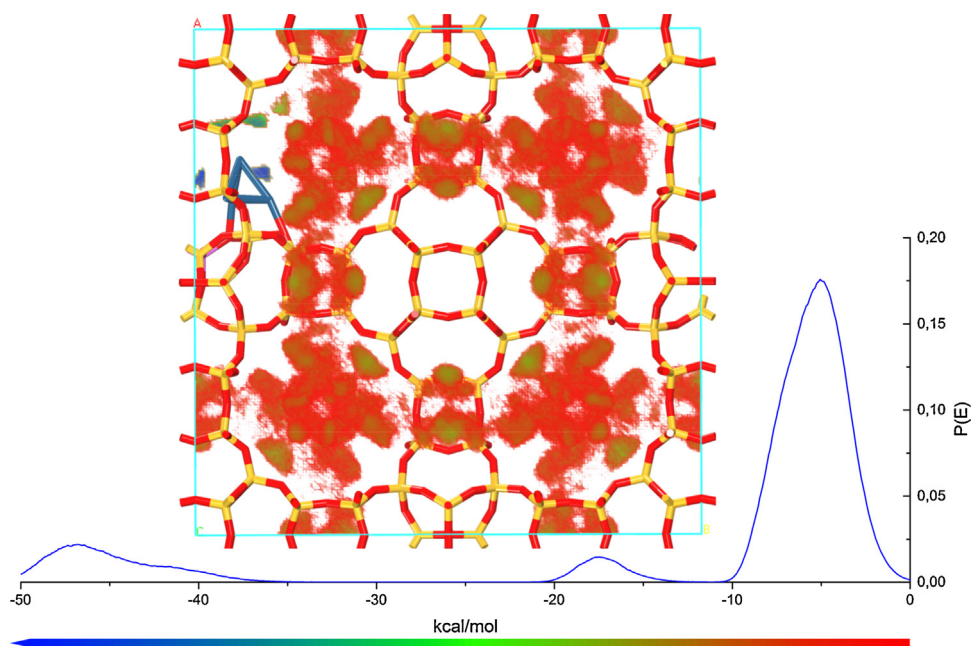
Fig. 6. Distribution of the CO_2 molecules in the porous system of IWS zeolite with one Ir_4 cluster (a) and representation of adsorption sites at the Ir_4 cluster (b).

Another extreme is the SBS zeolite. For this zeolite, the intuitive behavior is observed – in high pressure range the volume taken by the Ir_4 clusters does not allow to fit the additional molecules better, and adsorption is slightly worse than in case of pure zeolite (Fig. 7).

This can be only analyzed together with the mass clouds. The Ir_4 cluster in EMT zeolite is located in the space, which is in pure-silica EMT occupied by the main part of the mass cloud. The presence of the cluster strongly distorts the cloud, because adsorption at the Ir_4 cluster occurs only in specific, strictly localized adsorption sites and regardless of the zeolite framework. On the other hand, the porous volume occupied by the cluster is not important in the low pressure range, when the adsorption to pure zeolite barely takes place, and only strong adsorption centers available are those on the Ir_4 cluster. In high pressure range, there is a competition between the cluster together with the chemisorbed molecules and a number of physically adsorbed molecules. The number of physically adsorbed CO_2 molecules in this volume depends on the pressure and at some pressure magnitude those two numbers match, what is visible on the isotherms where the curves tend to cross.

In contrast to this, the cluster in SAO zeolite is settled in the space which is less significant for physical adsorption, what can be observed by only minor mass cloud distortion. This system gains the adsorption capacity in low pressure range by the same mechanism as EMT, however at high pressure it behaves differently. The physical adsorption is less preferred in the volume occupied by the cluster, what means that in high pressure range there is no competition between CO_2 molecules in this area.

The correlation between mass cloud distortion, caused by the presence of the cluster, and the shape of the isotherms extends also on other investigated zeolite frameworks. In the case of SBT zeolite (Fig. 8a), where the effect of mass distortion is an intermediate between EMT and SAO, also the isotherm curves exhibit an intermediate trend. Admittedly, the difference in adsorption capacity decreases with the pressure, however less intensively and the curves are unlikely to match at high pressure values. Similar isotherm pattern is observable for IWS zeolite (Fig. 8c), in which the mass cloud distortion is comparable to EMT, whereas SBS zeolite (Fig. 8b) takes the "fading" isotherm pattern.
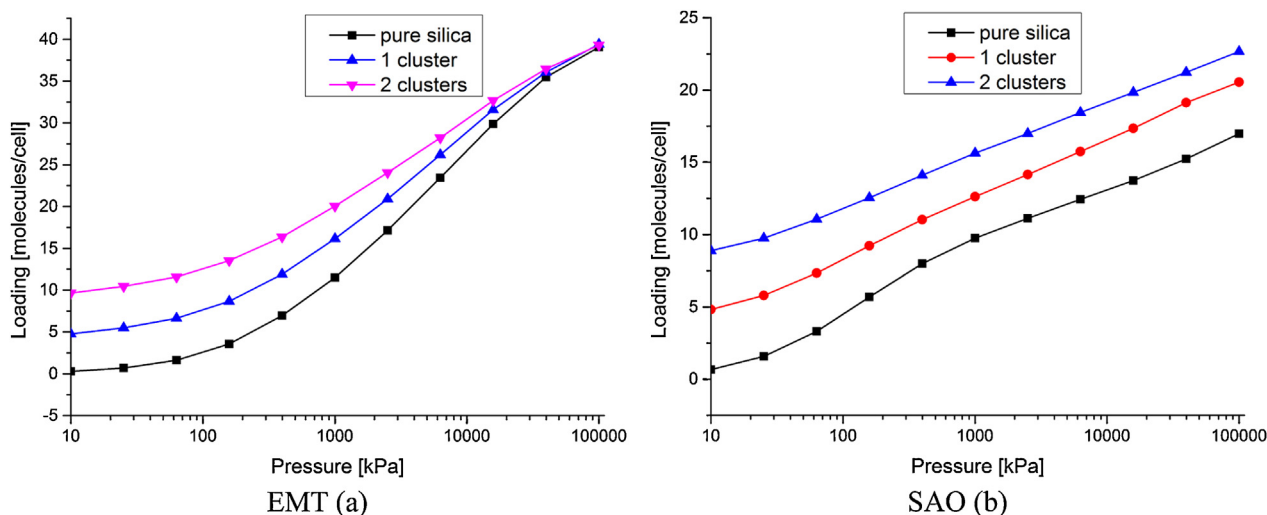

EMT (a)

SAO (b)

Fig. 7. Adsorption isotherms for pure-silica, single cluster and double cluster per cell EMT (a) and SAO (b) zeolites.
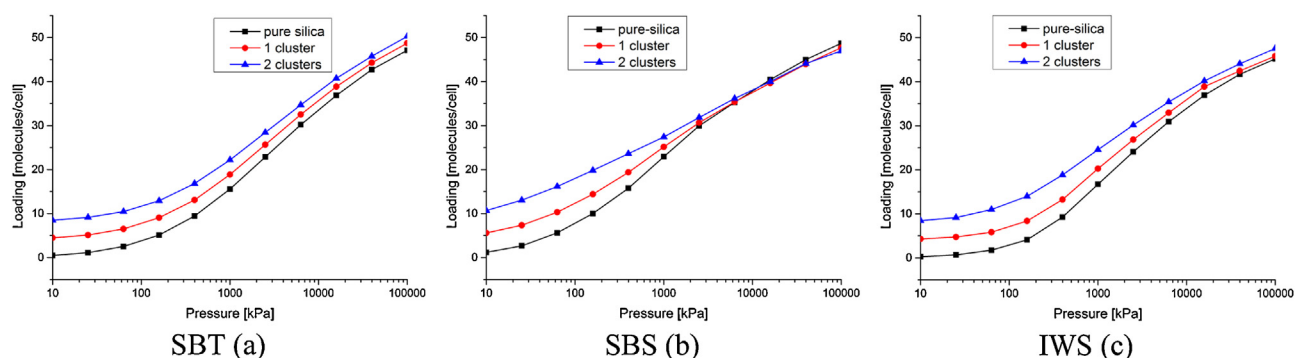
Fig. 8. Adsorption isotherms for pure-silica, single cluster and double cluster per cell SBT (a) and SBS (b) and IWS (c) zeolites.

5. Conclusions

In this study, we have investigated adsorption of carbon dioxide molecules on selected zeolites containing Ir_4 clusters, by making use of the GCMC method.

It was found that adsorption of carbon dioxide on Ir_4-enhanced zeolites preserves common general character on all studied zeolite frameworks, which is increasing the adsorption capacity by the cluster, and the presence of localized adsorption sites at the cluster. However, dependent on the zeolite framework type, the cluster occupies a part of porous volume, which is more or less significant for physical adsorption. In consequence, the cluster introduces individual adsorption site which, locally, in a greater or lesser extent, disturbs the main type of adsorption. Thus, the location of the cluster in the zeolite structure, and in fact, toward the mass cloud, is crucial. In this work, we have presented three different cases: significant perturbation of the mass cloud by the presence of cluster (EMT, SBS), minor perturbation of the cloud (SAO) and an intermediate case (SBT, IWS).

This effect directly correlates with the shape and trend of the adsorption isotherms, where two patterns can be distinguished. One of them, in which the increased adsorption capacity is preserved in the whole pressure range, represents the system, where the cluster only subtly perturbs the mass cloud (SAO). The other is just the opposite one – the cluster distorts the cloud rapidly and the difference in adsorption capacity fades with the pressure up to reaching a point where the isotherms tend to match (EMT, SBS). In an intermediate case the difference decreases with the pressure, however less intensively and the curves are unlikely match (SBT, IWS).

Coexistence/competition of those two adsorption types: physisorption on the zeolite and local, strong adsorption at the clusters, exhibits a correlation with the shape of adsorption isotherms. Investigated system is a case, in which an adsorbent is modified by introducing extra, most preferable adsorption sites, where a distinct type of adsorption takes place. This is not a unique case, thus one can expect that our observations are preserved not only for presented zeolite supported iridium, but also for a wider range of materials, including different metals supported by zeolites or even different supports. Crabtree et al. [38] have suggested, that the surface adsorption of CO_2 on faujasite is more affected by the surface structure than the composition, which allows to suspect that our observations may be transferable to wider group of materials.

Modification of zeolites by introduction of iridium clusters allows to obtain a material, that exhibits enhanced adsorption properties particularly in low pressures, however optimal selection of zeolite structure and adjusting of location of the cluster in the framework enables to design a system, which preserves increased adsorption capacity also in high pressures. Keeping in mind, that tetrairidium cluster has been proven to be able to chemisorb/activate CO_2 molecules, and at the same time, to perform hydrogen spillover process, zeolite-supported Ir_4 may be also a potential precursor for an active catalytic system.

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