Two-dimensional topologies and clustering on zeolite surfaces.
A Monte Carlo study

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Monte Carlo simulations were carried out to investigate the clustering of adatoms on zeolite surfaces. The zeolite surface is built up by repeated template which models the smallest building unit. The movement of each adatom is then monitored by a random walk algorithm. Lateral interactions beyond nearest-neighbor interactions are considered. Eight types of zeolite surfaces were used to demonstrate the influence of pore size and topology on the clustering rate. Zeolite with larger pore size is found to have a lower clustering rate. Higher symmetry of zeolite surface topology instead leads to a higher clustering rate.

1. Introduction

Dynamical processes occurring in restricted geometries [1,2] such as polymers [3,4], clays [5], micelles [6], zeolites [7] and other molecular assemblies [8] have recently been under extensive investigations due to their importance in catalytic and separation processes. Computer simulation using molecular dynamical techniques [9] or Monte Carlo methods [10] has been recognized as a useful tool in exploring our understanding in this respect. In this Letter we would like to address some interesting findings in our recent study of clustering processes on zeolite surfaces using a Monte Carlo scheme.

Immense efforts were made to explore the effects of clustering among adatoms on various aspects of surface processes, such as reaction kinetics [11,12], thermal desorption spectra [13,14], chemisorption [15], laser-induced thermal desorption [16], and deactivation of supported catalysts [17]. Most of the simulations were performed on a regular model surface such as a square lattice, hexagonal lattice and trigonal lattice and can be rationalized within the Ising model with nearest-neighbor interactions [11-13,15,16]. Effect of lateral interactions beyond nearest-neighbor interactions on the lattice gas model were recently reported by several authors in their study of the gas–surface processes. For instance, Zhdanov and co-workers [14] replaced the mean-field, the quasi-chemical or the Bethe–Peierls approximations [18–25] by an approximation including the next-nearest-neighbor interactions in addition to the nearest-neighbor interactions. Lee et al. also reported the inclusion of lateral interactions beyond nearest-neighbors in the simulation of island formation over a square lattice [26].

Zeolite surfaces provide a lot of varieties in spatial pattern and topology [27] which would not be found on regular surfaces. The key difference between a zeolite surface and a regular surface is the spatial inhomogeneity caused by the polygonal constituents and varying pore sizes composing a zeolite surface. The consequence of the spatial inhomogeneity is reflected in the movement of each adsorbate which would subject to an anisotropic lateral interaction. These facts make the simulation of such a many-body
problem, i.e. clustering, on the zeolite surface a comparatively difficult task. Note that most simulations in the zeolite science were concentrated on adsorbate–zeolite interactions and were performed within a host-plus-one-guest-molecule framework [28–35]. In our first try to model the mordenite surface, we used an algorithm, which was called the spectrum method, in which the lattice points were divided into several classes according to the similarity of their neighboring environments [36]. Such an algorithm was soon found to be inconvenient as applied to other zeolite surfaces. Recently we developed a general strategy [37], called template method which can be easily extended to treat various zeolite surfaces. A brief introduction of this algorithm will be given in section 2.

Eight types of surfaces including seven zeolite surfaces and a graphite surface were chosen in this work in order to study the effect of spatial inhomogeneity on clustering on zeolite surfaces. Results of our simulations will be presented and discussed in section 3. Conclusions are then drawn in section 4.

2. Method and model

A zeolite surface is, in general, not a flat surface. For our purpose, it is used to be projected along a certain direction, say [100] for a AlPO₄-25 as shown in ref. [27]. In the text, a zeolite surface should hereafter be referred to as a projected flat surface with suitable topology of a selected zeolite surface. As mentioned earlier, such a surface is quite different from a regular lattice surface, such as a square lattice, triangular lattice and honeycomb lattice, due to the coexistence of more than two types of polygons on a surface plane. Among the three regular surface lattice models, only on the honeycomb lattice has each lattice point the same connectivity as that on the zeolite surface, i.e. each lattice point has three nearest-neighboring lattice points. Therefore, the graphite surface is chosen for comparison in our simulations.

The zeolite surface is modeled by an array of $N \times M$ templates, where $N$ and $M$ are the number of templates along the $x$ and $y$ axes used to construct the lattice model. A template is the smallest unit from which a zeolite surface can be built. The templates used to build a mordenite surface and a ferrierite surface are shown in fig. 1. In this scheme, each lattice point is coded in a three-dimensional array $(i,j,k)$, namely, this particle is on the $(i,j)$ template and the $k$th lattice point in that template. The fundamental coding unit requires $3 \times 3$ blocks, namely, for a particle sitting on top of a lattice point in a template one should know how this particle will move according to the connection of the lattice to the relevant lattices in the surrounding eight templates. For detailed description of this algorithm, one should refer to ref. [37].

Only one adsorbate is allowed to occupy a lattice position, i.e. a lattice site could be empty or occupied by a single adsorbate. The adsorbate is assumed to be located on top of the lattice site only. Hence, it is basically a two-dimensional lattice gas on a non-simple regular lattice model, i.e. the three-dimensional nature of adsorbates would not be included in this model. Also, the multilayer problem was not considered in our current study.

Interaction potentials among adsorbates are not given a specific form and are assumed to be $r^{-q}$ dependent, where $r$ is the separation between a pair of adsorbates and $q$ is taken to be 2. Besides, the interaction energy is taken to be a dimensionless parameter in units of $kT$, where $k$ is the Boltzmann constant and $T$ is the system temperature which is kept the same during each simulation. The energy parameters for nearest-neighbor interaction and adsorbate–lattice interaction are assumed to be 2 and 1, respectively. Next-nearest-neighbor interaction energies among next-nearest-neighbors sitting on a given polygon are computed for various types of polygons and are collected in table 1.

In most calculations, the number of adsorbates is

(a) (b)

Fig. 1. Template unit used for building the surfaces of (a) ferrierite and (b) mordenite in our simulations.
Table 1
Parameter values and next-to-nearest energy terms a)

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Grid size</th>
<th>No. of adatoms</th>
<th>Next-to-nearest energy terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>ferrierite</td>
<td>60 x 10 x 24</td>
<td>500</td>
<td>$E_5, E_6, E_{10}$</td>
</tr>
<tr>
<td>mordenite</td>
<td>60 x 15 x 16</td>
<td>500</td>
<td>$E_4, E_5, E_6, E_{12}$</td>
</tr>
<tr>
<td>mazzite</td>
<td>60 x 7 x 36</td>
<td>500</td>
<td>$E_5, E_6, E_8, E_{14}$</td>
</tr>
<tr>
<td>graphite</td>
<td>60 x 60 x 4</td>
<td>500</td>
<td>$E_6$</td>
</tr>
<tr>
<td>AlPO4-25</td>
<td>60 x 13 x 18</td>
<td>500</td>
<td>$E_4, E_5, E_8$</td>
</tr>
<tr>
<td>AlPO4-11</td>
<td>60 x 24 x 10</td>
<td>500</td>
<td>$E_4, E_5, E_{10}$</td>
</tr>
<tr>
<td>AlPO4-5</td>
<td>60 x 40 x 6</td>
<td>500</td>
<td>$E_4, E_5, E_{12}$</td>
</tr>
<tr>
<td>AlPO4-8</td>
<td>60 x 20 x 12</td>
<td>500</td>
<td>$E_4, E_5, E_{14}$</td>
</tr>
</tbody>
</table>

a) The interaction energy between nearest-neighbor adatoms is assigned to be $2kT$. The subscript of each next-to-nearest energy term stands for the edge number of polygon and the energy term is the interaction potential for a pair of adatoms locating on the next-to-nearest neighboring sites of such a polygon.

$E_4 = 1.000kT$, $E_5 = 0.764kT$, $E_6 = 0.667kT$, $E_8 = 0.586kT$, $E_{10} = 0.553kT$, $E_{12} = 0.536kT$, $E_{14} = 0.526kT$.

taken to be 3%–4% of the number of lattice sites. The adsorbates are initially randomly distributed over the square lattice to keep the particle distribution approximately fully dispersed. Each adsorbate can then make a move from a lattice position $(i, j, k)$ to a new lattice position during one Monte Carlo step (MCS) with the probability

$$P_{\infty} \exp(-E)$$

which is governed by $E$, the total interaction energy of this adsorbate with its neighboring adsorbates as well as the surface atom

$$E = E_{ij} + \sum N_n E_n + N_m E_m,$$

where $E_{ij}$ is the interaction energy between the adsorbate and the surface atom, $E_n$ is the interaction between the adsorbate and its nearest neighbor and $N_m$ is the number of its nearest neighbors, and $E_n$ is the next-to-nearest-neighbor interaction energy of the adsorbate and its next-nearest neighbor sitting on the $n$-membered ring and $N_n$ is the number of next-nearest neighbors in the $n$-membered ring. The probability for this adsorbate to stay at the original lattice during a MCS is thus proportional to $1 - P$. For a random walker, each of the three-nearest-neighbor positions is assumed to be an equally probable site. The a priori probability of moving from position $(i, j, k)$ to one of the three nearest-neighbor sites is $P/3$. The position of the adsorbate becomes entering the next MCS is determined from the product of four random numbers $r_1, r_2, r_3, r_4$ chosen from a uniform distribution with the four probabilities associated with the four possible outcomes, i.e. three of them for movement along three directions and one for no move. If the adsorbate is decided to move, it will move to its new position unless this new position is occupied. The maximum value among the four products $(r_1P/3, r_2P/3, r_3P/3, r_4(1 - P))$ would fix the destination of the adsorbate. Periodic boundary conditions are imposed at the outer edges of the lattice to guarantee that no net diffusion flux moves out of the model surface.

One should note that all of the adsorbates do not move simultaneously, instead each adsorbate moves sequentially. However, for each MCS the sequence of the adsorbates is randomly adjusted so that every adsorbate has an even possibility to move first. In each simulation, $10^6$ MCS were made. Positions of adsorbates and the extent of aggregations were recorded and analyzed every $10^5$ MCS. For our purpose, only the time evolution of average cluster size is presented in this Letter.

3. Results and discussions

Eight types of model surfaces used in our simulations are displayed in fig. 2. These eight surfaces were chosen to demonstrate the effect of topology on the clustering process among adsorbates. Among them, members of the AlPO4 family have different pore sizes ranging from 8, 10, 12 to 14 edges, the other four possess different symmetric features in their outlooks. Simulations were performed on these surfaces with the initial coverage of 3.30%–3.47%, in a $10^6$ MCS period with the interaction parameters as listed in table 1. The clustering rate is then analyzed by computing the average size per cluster as time proceeds.

Surfaces of members of the AlPO4 family are constructed from four-, six-membered rings, and the characteristic pore. The major differences in the interaction energies, which control the movement of the adsorbate, come from the next-nearest-neighbor interactions in the characteristic pore. Thus, it can be expected that larger pore size would favor the more dispersed distribution among adsorbates. Our sim-
Fig. 2. Eight types of model zeolite surfaces used in our simulations. They are surfaces for (a) AlPO₄-25; (b) AlPO₄-11; (c) AlPO₄-5; (d) AlPO₄-8; (e) ferrierite; (f) mordenite; (g) mazzite; and (h) graphite.

Simulations show that this is indeed the case.

In fig. 3, the average cluster sizes on the surfaces of the AlPO₄ family are plotted as a function of MCS. The average cluster sizes for these four cases are initially approximately equal to one due to initially fully dispersed distribution of adsorbates. The clustering processes are found to occur within $10^5$ MCS as can be seen in fig. 3. The 14-membered ring AlPO₄-8 is found to have the lowest final average cluster size of a value of 3.18 adatoms after $10^6$ MCS. The 12-membered ring AlPO₄-5 is found to have an average cluster size of 3.63 adsorbates at $10^5$ MCS and aggregates further to an average cluster size of 4.75 adatoms after $10^6$ MCS. As the pore size is getting smaller and smaller as in the case of AlPO₄-11 and AlPO₄-25, the clustering rate is found to be increased as can be seen from fig. 3. As mentioned earlier, members of the AlPO₄ family are composed basically of 4-, 6-membered rings and the characteristic large pore, it could be concluded that the large pore size of a zeolite surface tends to reduce the clustering rate of the adsorbates.

Effects of symmetry of surface configurations on clustering is demonstrated by performing $10^6$ MCS simulations on mordenite, ferrierite, mazzite and graphite surfaces with the selected interaction parameters listed in table 1. A plot of the average cluster size as function of MCS for these four model surfaces is presented in fig. 4. As can be seen from fig. 4, the graphite surface is found to cluster quite extensively to an average size of 8.51 adsorbates at $10^5$ MCS and the clustering progresses to an average value of 19.23 adsorbates. The regular shape of the lattice seems to facilitate the clustering process. Note that in our previous report [26], clustering on the honeycomb lattice is less extensive than that on the square lattice, using the same set of interaction parameters and the same initial coverage. In the case
Fig. 3. Plot of average cluster size as a function of MCS for surfaces of AlPO₄ family members; (◇) AlPO₄-25, (+) AlPO₄-11, (■) AlPO₄-5, (△) AlPO₄-8.

Fig. 4. Plot of average cluster size as a function of MCS for surfaces of (◇) ferrierite, (△) mordenite, (+) mazzite and (■) graphite.

of the ferrierite surface, the 10-membered-ring pore is surrounded by five- and four-membered rings. The outlook of the ferrierite surface is less symmetric with respect to that of the graphite surface, the average cluster size is 5.03 adsorbates at 10⁵ MCS and 8.83 adsorbates at 10⁶ MCS. The clustering process proceeds in a quite similar manner as it occurs on the AlPO₄-11 surface, which also has a 10-membered-ring pore. The mordenite surface has an even less symmetric outlook due to the lengthening along one direction as one more edge is added to this direction. It can be easily seen from fig. 4 that the clustering process proceeds less extensively as reflected by the average cluster size of 3.57 adsorbates at 10⁵ MCS to 4.82 adsorbates at 10⁶ MCS. Clustering on the mordenite surface is found to be similar to that on...
the AlPO₄-5 surface which also has a 12-membered ring hole. As for the mazzite surface which has the least symmetric appearance among the eight model surfaces, we found that the clustering occurs very scarcely as reflected by the average cluster size of 2.57 adsorbates at 10⁵ and at 10⁶ MCS. The clustering on the mazzite surface is less extensive than that on the mordenite surface, which also has a 12-membered ring pore, and is even less than that on the AlPO₄-8 surface, which has a 14-membered ring pore. Therefore, symmetry of the outlooks of zeolite surfaces could also affect the clustering process occurring on them. Detailed analyses of these simulations will be published elsewhere.

4. Conclusions

Monte Carlo simulations were performed for low surface coverages of approximately 0.03 to investigate the clustering in a submonolayer of adsorbates on eight types of zeolite surfaces. The less symmetric outlooks of zeolite surfaces with respect to that of a graphite surface are found to reduce the clustering rate in general. Simulation results from the AlPO₄ family concluded that larger pore size on the surface would lead to lower clustering rate. Comparison among the clustering rates of graphite, ferrierite, mazzite, mordenite and AlPO₄-8 found that higher symmetry of zeolite surface topology would result in a higher clustering rate.

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