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Modeling of Organically Functionalized Mesoporous Silicas for the Design of Adsorbents

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Abstract. In order to obtain atomic-level models for hybrid inorganic-organic adsorbents that are based on ordered mesoporous silicas, molecular simulation methods have been developed which follow the reaction path of the synthesis of the silica material in a kinetic Monte Carlo Simulation. Organic surface groups such as phenyl or aminopropyl are introduced by replacing surface hydroxyl groups. The adsorption in these models is simulated by Grand Canonical Monte Carlo simulation. The experimental and simulated adsorption isotherms of ethane and carbon dioxide on MCM-41-based hybrid adsorbents agree well. In combination, these methods enable the computer-aided design of hybrid inorganic-organic adsorbents.

Keywords: mesoporous silica, MCM-41, functional groups, adsorption, molecular simulation

1. Introduction

Ordered mesoporous solids of various pore sizes and shapes can readily be prepared with organic functionalities lining the silicate framework, by co-condensation of triethoxysiloxanes, or afterwards by grafting the desired triethoxysiloxane to the surface of the pure-silica material (Garcia-Bennett et al., 2002; Fowler et al., 1997). Surface chemistry and pore geometry are two governing factors with respect to the adsorption properties of a porous material. It should therefore be possible, by careful choice of the functional group, to tailor the properties of such an inorganic-organic hybrid material to effect separations of various gas mixtures.

To identify potential adsorbent structures by computer simulation it is necessary to predict their adsorption behavior, which we do by Grand Canonical Monte Carlo (GCMC) simulation. However, GCMC simulations require atomic-level models of the adsorbent and, in contrast to crystalline materials such as, zeolites a full experimentally based description of the location of the atoms is not possible for the amorphous structures of ordered mesoporous silicas. We do this by simulating the hydrothermal synthesis and the calcination of ordered mesoporous silica. It generates models of the pure silica structures which are then modified by replacing surface silanol groups by a model of the desired surface modification.

2. Computational Methods

2.1. Kinetic Monte Carlo Simulation of the Synthesis

Molecular dynamics simulations are not suitable for the simulation of the synthesis of mesoporous silicas since the number of atoms involved in combination with the slow reaction rate cannot be covered with computers available today. To overcome this, a kinetic Monte Carlo (KMC) scheme has been developed, which is independent of real reaction time and uses simple atomic interaction potentials. In the KMC simulation, every simulation step corresponds to a reaction step (Kasehagen et al., 1997; Rankin et al., 2000). Obeying the relative kinetics observed during the real polymerization reaction (Assink and

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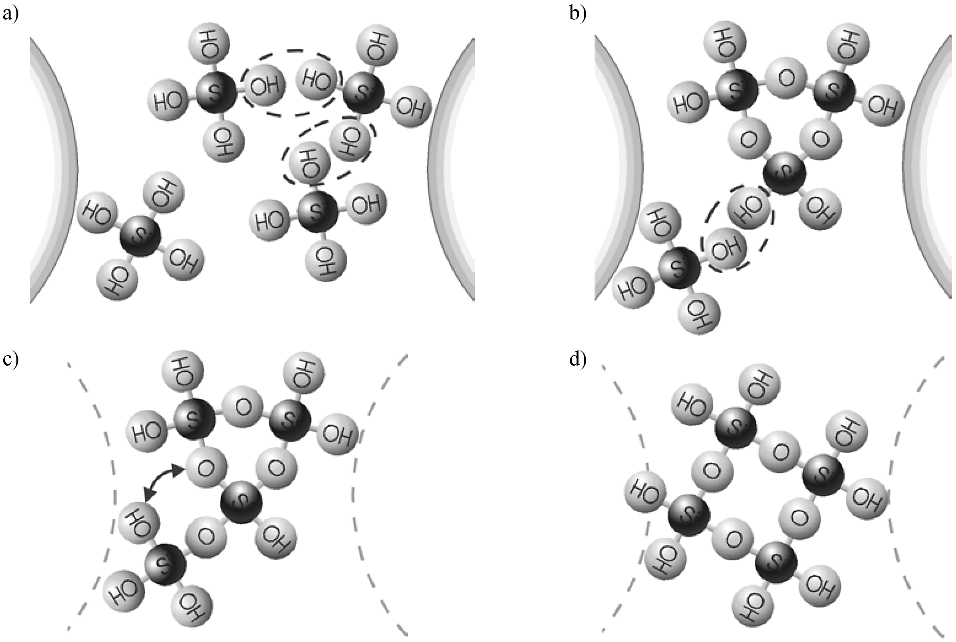

Figure 1. Schematic representation of the steps in a KMC simulation. (a) Silicic acid monomers near micelles. Dashed circles show possible condensation reactions (b) Further condensation and formation of rings. Bridging oxygen atoms can be hydrolyzed. (c) Calcination: the arrow indicates switching of a siloxane bridge to relax the ring. Dashed lines show the former positions of the templates. (d) Refined structure after calcination.

Kay, 1988), silica monomers are linked step-by-step to form an amorphous network to follow the reaction path of the real synthesis. The hydrolysis of siloxane bridges and the switching of bridges between neighboring silicon atoms of the amorphous network are also possible. See Fig. 1 for a schematic representation of the possible KMC reaction steps. Water molecules which participate in condensation and hydrolysation reactions are not modeled explicitly in the simulation. It is assumed that the diffusion rate of water molecules through the thin walls towards the pore volume is high compared to the reaction rate of the polymerization.

The energy of the formation of a siloxane bridge from two neighboring silanol groups was set to -13.4 kJ/mol according to quantum mechanical calculations for the reaction of two silicic acid monomers to a dimer in aqueous solution (Catlow et al., 1997). During the simulation of the hydrothermal synthesis, the reaction is reversible, while in the following simulation of the calcination at high temperature, the siloxane bridges cannot be hydrolyzed to reflect the lack of water present during the calcination.

In the KMC scheme, the reaction steps are performed as trials that are then accepted or rejected with a probability according to the change of energy they cause, generating a Boltzmann distribution of the total energy of the system. Simple models are applied to describe bonded and non-bonded interactions. Covalent bonds between silicon and oxygen atoms are modeled by harmonic spring potential functions, optimized to reproduce elastic properties of amorphous silica (Tu and Tersoff, 2000). Non-bound atoms interact with a soft repulsive potential of a shape similar to the repulsive part of a Lennard-Jones potential of an oxygen atom. The strain energies in small silica rings close to the values obtained from *ab initio* calculations (Uchino et al., 2000). Silicon atoms and oxygen atoms are modeled explicitly. Hydrogen atoms are not taken into account directly, therefore the simulation does not distinguish between protonated and deprotonated forms silanol groups and the influence of the pH of the synthesis solution has to be taken into account implicitly in the reaction rates. The models for the templating micelles are attractive to nearby oxygen atoms, but repulse them if they penetrate into the template. The repulsion is soft enough to allow for small deformation micelle models.

The periodically replicated simulation volume is of the shape of a parallelepiped with fixed angles but of varying size. The lengths of the edges are adjusted to achieve the equilibrium of outside pressure and strain inside the cell. Using the methods and potentials described above, the KMC simulation starts from a templating micelle which becomes covered by a partly condensed silica layer by adding silicic acid molecules. The number of monomers determines the wall thickness of the final structure. Then multiple images of the silica covered micelle are arranged in an infinite periodic array and pushed together so that they agglomerate to mimic the supposed mechanism of the formation of the regular phase (Corma, 1997). For MCM-41-like structures it was found that a deformation of the micelle towards a hexagonal shape at this stage of the simulation yields a better final result than if the micelle stays circular in shape. The simulation of the polymerization continues until it has reached equilibrium, i.e., the number of formed siloxane bridges does not increase further.

The hydrothermal synthesis at ambient temperature is followed by the calcination at elevated temperature. The condensation reaction is now irreversible, but siloxane bridges can still switch between neighboring silicon atoms. The model micelles are removed from the simulation and silica network condenses further. Finally, the temperature is decreased step-wise back to ambient temperature and one obtains the model of the ordered porous silica.

2.2. *Placement of Surface Groups*

Organic surface groups are introduced to the model generated by the KMC simulation by substituting the silanol groups of the pure-silica model with the desired organic functional group. The types of surface groups used in this work are depicted in Fig. 2. A random but energetically favorable distribution of the surface groups across the pore walls is achieved by swapping the positions of the surface groups in a Monte Carlo scheme.

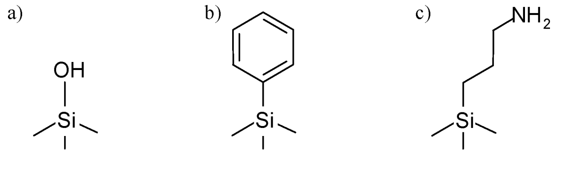

Figure 2. (a) Silanol group, (b) phenyl group, and (c) aminopropyl group attached to a silicon atom in the silica framework.

2.3. *Grand Canonical Simulation of the Adsorption*

The adsorption properties of the model mesoporous silica are determined in GCMC simulations. The silicon and oxygen atoms of the silica structure are kept fixed throughout the GCMC runs. The surface groups such as phenyl or aminopropyl groups are modeled as flexible chain molecules which are fixed to the wall.

The van der Waals interaction between atoms of the adsorbent, surface groups, and gas molecules are represented by Lennard-Jones potentials. For combinations of different species, the Lorentz-Berthelot combination rules were applied. Electrostatic interactions are taken into account by effective point charges and their coulombic potential is calculated using Ewald summation in three dimensions. Bond stretching, bending, and torsion in chain molecules is described by harmonic potential functions and a Fourier series, respectively. Chain molecules are handled using a dual-cut-off configurational-bias Monte Carlo method (Vlugt et al., 1998).

Potential parameters for helium, ethane and carbon dioxide are available in the literature (Talu and Myers, 2001; Fischer et al., 1987; Bakaev et al., 1999). For phenol as a non-polar surface group and ethane as a non-polar adsorbate, the silicon and hydrogen atoms of the silica structure are neglected and the interaction of the fluid or surface group with the silica framework is described by an effective Lennard-Jones potential for the oxygen atoms; this potential is transferable between different silica materials (Yun et al., 2002). The aromatic ring of phenyl is assumed to be rigid but the carbon-silicon bond can bend and the ring can rotate about it. For aminopropyl surface groups and carbon dioxide, a model with point charges and explicit silicon atoms (Brodka and Zerda, 1996) is used. The covalent bonds of the aminopropyl chain are allowed to bend and the atoms can rotate about them. Each CH_2 is represented by one pseudo atom, but the hydrogen atoms of the NH_2 group are modeled explicitly. The interaction between the NH_2 head group and carbon dioxide is assumed to be strictly physical. The partial charges on the atoms of these molecules are represented by effective point charges. The parameterization of the potentials for organic chain molecules is adopted from the optimized potentials for liquid simulations (OPLS) force field (Jorgensen et al., 1984, 1996; Stubbs et al., 2001) and the MM2 force field (Frierson et al., 1988).

To directly compare simulation results to experimental isotherms, the computed absolute amount adsorbed has to be converted to excess adsorption. The required value for the pore volume is obtained by the simulation of the adsorption of helium at low pressure as it is measured in the volumetric adsorption experiment (Talu and Myers, 2001).

3. Results and Discussion

3.1. KMC Simulations

Comparison of the evolution of the local coordination number of silicon atoms in the KMC simulation to H-NMR measurements of the polymerization of silicic acid in an acidic solution in ethanol and water in absence of templating micelles (Assink and Kay, 1988) shows good agreement with the experiment.

For MCM-41, the degree of polymerization after the simulation of the hydrothermal synthesis is close to the value measured experimentally by ^{29}Si-NMR (Gonzalez, 2004; Kleitz et al., 2003). Also the shrinking of the unit cell of MCM-41 upon calcination (Kleitz et al., 2003) is reproduced in the KMC runs. The final ratio of fully coordinated silicon atoms to silicon atoms that are still bound to one or two silanol groups, Q_4:Q_3, after simulation of the calcination reached 2.0, compared to ^{29}Si-NMR measurements of a calcined MCM-41 sample that showed a Q_4:Q_3 ratio of 4.0 (Kleitz et al., 2003). The lower degree of polymerization in the models is giving a higher number of silanol groups on the surface and/or inside the silica network of the walls. Simulations of the adsorption of small gas molecules showed that those regions of the silica wall where the agglomeration process caused the biggest deformation of the silica structure, tend to comprise small cavities which seem not to be present in the real material. This has been taken into account in further simulations of the adsorption by excluding the core of the thickest part of the wall from the GCMC simulation. Gas molecules are only allowed to penetrate the walls deeper than ca. 5 Å or half the wall thickness. The exact value has little influence on the adsorption isotherm since this region of the wall seems to be relatively dense. For ethane, this shifts the isotherm downwards by ca. 5%.

3.2. GCMC Simulations

Before the KMC method can be used to design an adsorbent for a specific separation task, the agreement between simulated adsorption isotherms and experimental isotherms for well characterized materials has to be confirmed. We chose the adsorption of ethane (an essentially non-polar species) and carbon dioxide (which has a significant quadrupole moment) on pure-silica MCM-41, on *in situ* phenyl-modified MCM-41, and on post-synthesis modified MCM-41 with amino-propyl groups. The ratio of surface groups to silicon atoms was about 0.1. The temperature was chosen to ca. −10°C where ethane and carbon dioxide both exhibit

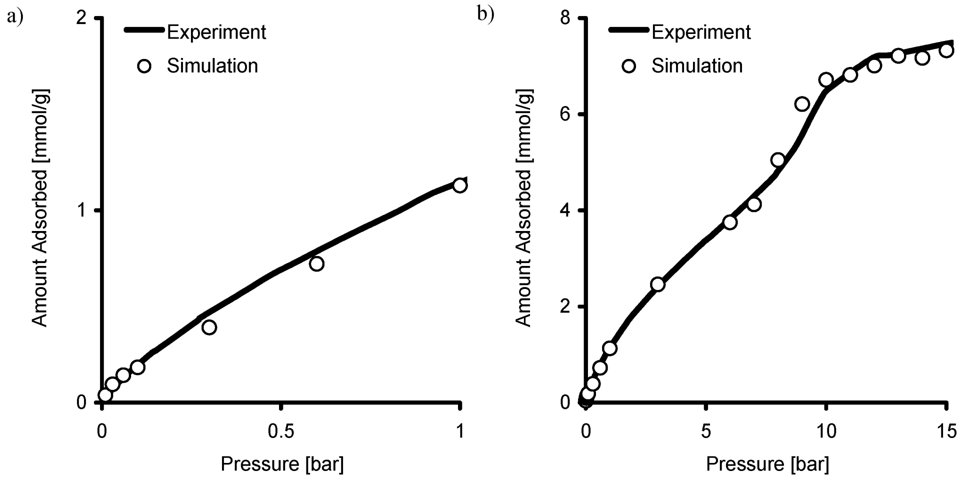

Figure 3. Experimental and simulated adsorption isotherm for ethane on pure-silica MCM-41 at 264 K. (a) The low-pressure region in more detail. (b) The whole pressure range up to pore filling. The experimental data are from He and Seaton (He and Seaton, 2003).

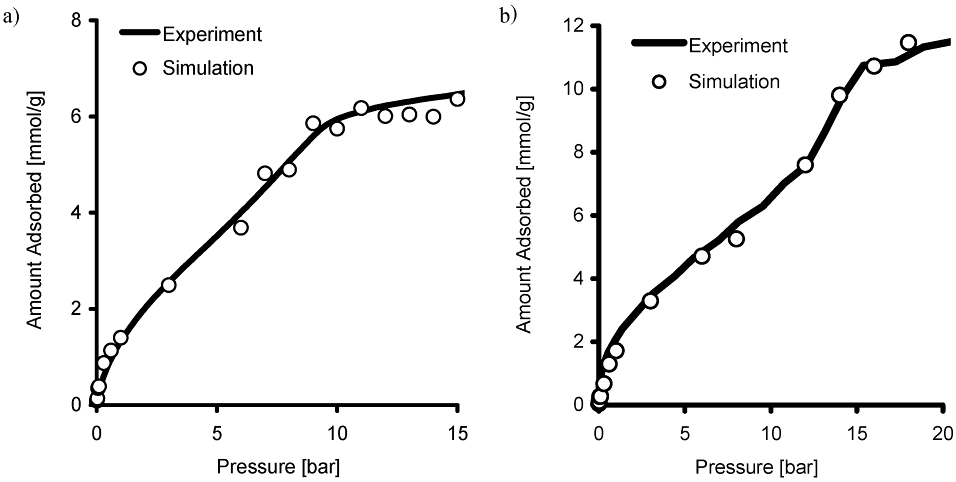

Figure 4. Experimental and simulated adsorption isotherms at 263 K (a) for ethane on in-situ phenyl-modified MCM-41 with a ratio of phenyl: Si = 0.1, and (b) for carbon dioxide on post-synthesis aminopropyl modified MCM-41 with a ratio of aminopropyl: Si = 0.1. The experimental data in (a) are from Perez-Mendoza (Perez-Mendoza, 2003).

type IV isotherms with a pore filling step below a pressure of 20 bars.

Figure 3 shows the isotherm for the adsorption of ethane on MCM-41. The agreement of simulation and experiment is good, except from a slight underestimation of the pore size which causes the pore filling to occur at slightly lower pressure in the model than in the real system. The isotherms of ethane on phenyl-MCM-41 and of carbon dioxide on aminopropyl-MCM-41 show also a good agreement, as illustrated in figs. 4(a) and (b) respectively. This is in particular remarkable for the latter system since the polar species are more difficult to model and no adjustments of partial charges were made, except where necessary to maintain neutrality of the system (the surface group models are taken from models for corresponding bulk molecules, thus partial charges have to be adjusted to balance the charges in the silica network).

4. Conclusions

A novel KMC method to simulate the synthesis of templated periodic mesoporous silica structures has been developed. The generated amorphous structures seem to be realistic, apart from fact that the degree of condensation inside the pore walls is slightly lower than the experimental value. Better understanding of the aggregation process and the refinement of the silica structure during calcination could help to modify the simulation method in a way that this problem does not arise anymore. So far we have circumvented it by excluding parts of the wall from the simulation of the adsorption. GCMC simulations of the adsorption of ethane and of carbon dioxide on pure-silica and on organically modified MCM-41 type structures, using the atom coordinates generated in the KMC simulation, reproduce the experimental isotherms across the whole pressure range.

The good agreement of simulation and experiment for the studied systems indicates that the methods we have developed should be able to predict the adsorption behavior of more complicated structures, e.g. SBA-1 or SBA-2, with more effective surface modifications, such as bulky phosphor ylides, sufficiently well for this approach to be used as a tool for the design of hybrid adsorbents for particular applications.

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