

Structure simulation of MCM-41 type materials

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Abstract

The structural properties of mesoporous molecular sieves with MCM-41 type structure were studied by molecular dynamics simulations. The ratio between wall thickness and pore diameter was varied and the stabilization energy of the lattice was determined for a pore diameter range between 15 and 49 Å. With decreasing wall thickness and increasing pore radius an increase of the stabilization energy was observed. Structures with partially interconnected pores and interrupted walls were found to be energetically unstable. Radial distribution functions indicated that the walls of MCM-41 type materials are preferably amorphous. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Mesoporous; MCM-41; Structure simulation

1. Introduction

Mesoporous molecular sieves with well defined pore sizes such as MCM-41 type materials, have become a class of substances with numerous applications in the field of catalysis, sorption, separation and sensor technology [1–4]. Although the structural properties of these mesoporous solids were extensively investigated over the last years [5,6] the structure of MCM-41 type materials on an atomistic level is still under discussion. This includes the shape of the pores and possible irregularities such as narrow sections or interconnections between the pores, the thickness of the walls and if the walls are amorphous or partially crystalline.

Only a few theoretical studies on MCM-41 type materials were presented up to now [7–11], while a comprehensive study describing the structure based on an unconstrained and energetically completely minimized model is still lacking. This might partially re-

sult from the large number of atoms necessary to describe the MCM-41 type structure without applying symmetrical constraints (i.e. ~3000–5000 atoms compared to 200–500 atoms usually needed for microporous molecular sieves and zeolites), but also from the question to which extent the structure is crystalline and thus how the selection of the starting geometry affects the results obtained in the simulation.

In this paper, we describe the structural properties of MCM-41 type materials using the results of a molecular dynamics study based on force field techniques. Structures with different pore diameters were used and the question how the shape of the pores and the thickness of the walls as well as their crystallinity influences the structural stability of MCM-41 type materials is discussed.

2. Theoretical methods

2.1. Construction of the initial structures for simulation

The structure of MCM-41 type materials consists of a hexagonal arrangement of one-dimensional cylindri-

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cal pores in the range between 25 and 100 Å [1,3]. The initial structure for the simulations was generated using the three-dimensionally infinite lattice of α -quartz and removing the atoms inside the pores of the diameter selected. The size of the hexagonal unit cell used was 49.1 Å \times 49.1 Å \times 27.0 Å, which allowed to vary the pore size during the simulations between 15 and 49 Å, without the necessity to generate a new unit cell for each model structure studied.

The pores and the internal surface, saturated with hydroxyl groups, were generated by the following procedure: (i) silicon and oxygen atoms located at positions inside the pores of the selected diameter were removed, (ii) vacant bonds on silicon atoms (i.e. Si atoms with less than four bonds to oxygen neighbors) were saturated with oxygen atoms and (iii) vacant bonds on oxygen atoms (i.e. O atoms with less than two bonds to Si atoms) were saturated with hydrogen atoms. Note that this procedure was chosen to exclude the generation of Si–H groups on the internal surface. An infinite lattice with MCM-41 type structure was generated using periodic boundary conditions on the unit cell applying P1 symmetry.

The pores of the initial structures were circular, their diameter was varied from 15 Å up to a diameter where the pore size was equal to the unit cell size, thus, generating discontinuities in the walls between the pores.

2.2. Simulation techniques

Due to the large number of atoms in the unit cell (\sim 2500–5000 depending on the pore diameter) force field techniques were used for the calculations. The energies were calculated from molecular dynamics simulations using Discover 2.9.8 and the cff91/czeol forcefield with parameters derived by Sauer et al. [12]. The simulations were carried out at a temperature of

700 K, using a time step of 1 fs and a simulation time between 1000 and 10,000 fs. Constant volume and constant temperature calculations were performed (NVT ensemble).

2.3. Determination of the stabilization energy

The stabilization energy (E_{stab}) of the MCM-41 type material was calculated from the total energy obtained in the simulation (Eq. (1)):

$$E_{\text{tot}} = n_{\text{Si}} \cdot E_{\text{Si-O}} + n_{\text{H}} \cdot E_{\text{H-O}} + E_{\text{stab}} \quad (1)$$

The energy contribution of the silicon-oxygen bonds ($E_{\text{Si-O}}$) was determined from the initial α -quartz structure by dividing the lattice energy (E_{SiO_2}) by the number of silicon atoms (n_{Si}) (Eq. (2)):

$$E_{\text{Si-O}} = \frac{1}{4} \left(\frac{E_{\text{SiO}_2}}{n_{\text{Si}}} \right) \quad (2)$$

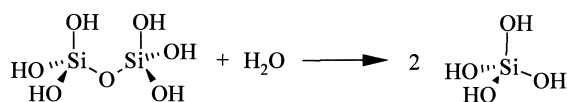
The energy for the formation of a hydroxyl group ($E_{\text{H-O}}$) was determined from the cleavage of a $(\text{HO})_3\text{Si-O-Si}(\text{OH})_3$ molecule and the subsequent addition a water molecule as shown in Fig. 1 and (Eq. (3)):

$$E_{\text{H-O}} = \frac{1}{2} (2E_{\text{Si}(\text{OH})_4} - E_{\text{Si}_2\text{O}_7\text{H}_6} - E_{\text{H}_2\text{O}}) \quad (3)$$

From this reaction an energy of $E_{\text{H-O}} = 25.11 \text{ kcal mol}^{-1}$ was determined for the formation of a hydroxyl group (Eq. (3)).

The stabilization energy of the mesoporous molecular sieves was calculated from the energy contributions given in the energy balance (Eq. (1)). The energy was normalized to the composition of the corresponding unit cell, because each model structure consisted of a different number of atoms.

$$E_{\text{stab}} = \frac{E_{\text{tot}} - n_{\text{Si}} \cdot E_{\text{Si-O}} - n_{\text{H}} \cdot E_{\text{H-O}}}{n_{\text{Si}}} \quad (4)$$



$$\Delta E = 50.21 \text{ kcal} \cdot \text{mol}^{-1}$$

Fig. 1. Structure to calculate the energy for the formation of a hydroxyl group.

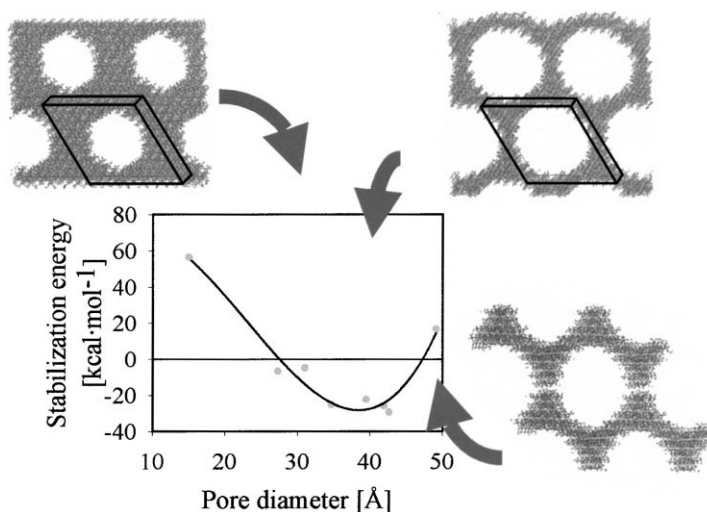


Fig. 2. Stabilization energy as a function of pore diameter.

3. Results and discussion

The stabilization energy together with models characteristic for the structures in the pore diameter range indicated is shown in Fig. 2. The concentration of hydroxyl groups and the stabilization energy as a function of the pore diameter is summarized in Table 1.

The stabilization energy showed a broad minimum at pore diameters between 35 and 42 Å. Structures with smaller pores and structures with pores that are not completely formed were found to be energetically not favorable. The wall thickness obtained for the most stable structures was in the range between 8 and 12 Å, which is in perfect agreement with the experimentally determined values between 7 and 15 Å [13,14]. These

results also confirm that a dense phase is the thermodynamically most stable structure of SiO₂ and that isolated Si(OH)₄ species are energetically not stable.

The concentration of hydroxyl groups on the internal surface was found to increase with the pore diameter. This results from the use of a constant unit cell volume and might be an artifact in this simulation, because the internal surface area increased with increasing pore diameter, while the wall thickness and consequently the total mass decreased. However, we would like to mention that the density of hydroxyl groups on the internal surface of MCM-41, prepared with C₁₂TMABr and C₁₆TMABr templates (determined by adsorption of pyridine followed by IR-spectroscopy [15]) was in the range of 0.8 mmol g⁻¹. Although there is not a perfect agreement between the experimentally determined concentrations and those resulting from the simulation, the numbers are in the same order of magnitude.

The radial distribution functions (RDF) between Si and O of the MCM-41 structure after optimization with a pore diameter of 42 Å, of crystalline α-quartz and amorphous glass are compared in Fig. 3. An example of the MCM-41 type structure with a pore diameter of 42 Å after the simulation is shown in Fig. 4.

Crystalline structures, such as α-quartz, are characterized in a radial distribution function by the presence of well defined distances between the atoms. On the

Table 1

Pore diameter (Å)	Stabilization energy (kcal/mol)	OH loading (mmol/g)
0.00	0.00	0.0
15.03	56.52	1.5
27.32	-6.76	2.7
31.05	-4.93	4.1
34.69	-25.15	4.9
39.50	-22.24	7.7
41.96	-25.82	9.0
42.64	-29.37	9.9
49.13	16.67	10.1

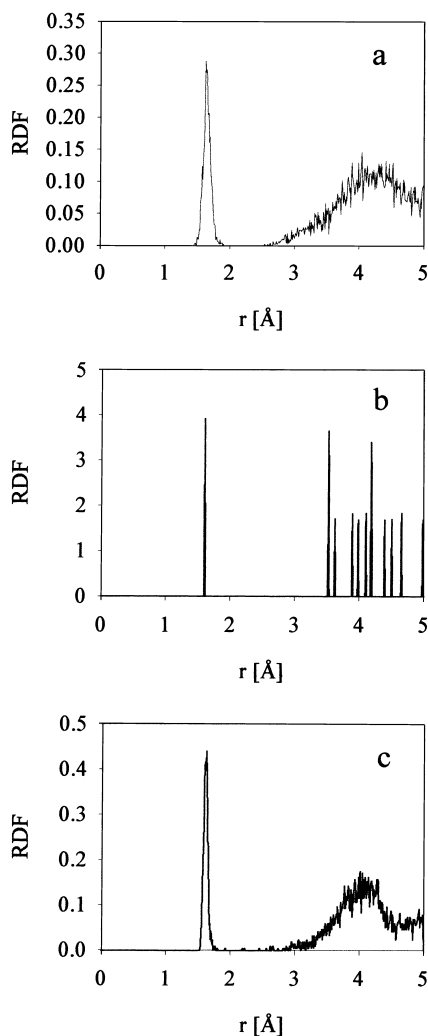


Fig. 3. Radial distribution functions of (a) MCM-41, (b) amorphous glass and (c) α -quartz.

contrary, radial distribution functions of amorphous structures show only well characterized Si–O distances to the nearest oxygen neighbors, while for the oxygen atoms at larger distances a broad distribution of distances is typically found. The radial distribution function obtained for MCM-41 after the structure optimization (see Fig. 3a) clearly indicates that the walls are amorphous. It is especially interesting to note that although a crystalline structure model was used as starting geometry the walls got less ordered during the molecular dynamics simulation.

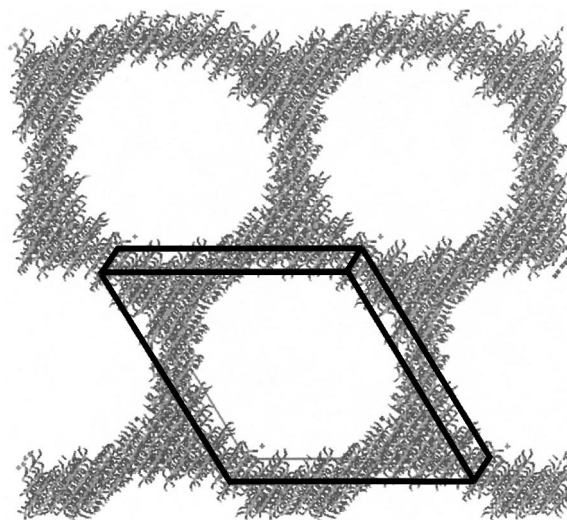


Fig. 4. MCM-41 structure with a pore diameter of 42 Å.

We would like to emphasize that for obtaining reliable results for the structure of MCM-41 type materials molecular dynamics simulations are essential to overcome local minima in the energy and to guarantee the flexibility necessary to reorganize the structure. Note, that this allows the use of a highly ordered (crystalline) model structure as starting structure for the simulations.

4. Conclusions

The results of the simulation indicate that for mesoporous molecular sieves of the MCM-41 type structure an optimum range for the pore size and wall thickness exist. With decreasing wall thickness the lattice energy decreases, i.e. the structure becomes more stable, until a pore size is reached where the walls become partially disconnected at their thinnest sections. The optimum wall thickness for MCM-41 type materials with a pore diameter in the range of 35 to 50 Å is predicted to be between 8 and 12 Å. The walls between the pores of MCM-41 are as thin as possible, however, the formation of interconnection between the pores is energetically highly unfavorable. For all structures studied the simulation indicated that the walls are preferably amorphous and the pores are slightly hexagonal.

Acknowledgements

The work was supported by the “Fonds zur Förderung der Wissenschaftlichen Forschung” under project P10874 CHE.

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