MOLECULAR MODELING OF HMS HYBRID MATERIALS FOR CO2 ADSORPTION

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Introduction

Hexagonal mesoporous silicas (HMS) and related structures (MCM-41, SBA-15, etc) which have long-range periodicity, yet poorly defined short-range order, possess very high surface areas and well hydroxylated surfaces that are amenable to functionalisation.

The grafting, or tethering, of organic groups onto the surface leads to novel inorganic-organic hybrid materials with a variety of potential applications in gas separation, selective adsorption, sensing devices, microelectronics, non-linear optical devices, etc[1].

Surface functionalisation by alkylamino groups is of particular interest, since interactions between the basic surface which is formed and mildly acidic CO_2 molecules may provide a means of selectively adsorbing and separating CO_2 from combustion (flue) gas streams[2].

This molecular modeling study was commenced to aid the synthesis and design of such hybrid materials, by providing insight into the geometric constraints and the molecular mobility limitations that apply: (a) when functionalising reagents are brought into proximity of mesoporous silica surfaces and (b) during adsorbate-adsorbent interactions after surface functionalisation.

Experimental

This molecular dynamics (MD) study made use of the Materials Studio[3] suite of programs, in particular the molecular simulation program *DISCOVER* and the *COMPASS* forcefield[4].

MD runs were carried out using a 1 fs time-step. Equilibration runs (typically 10,000 steps) were carried out prior to production runs of 100,000 steps (total of 100ps). Simulations were carried out at constant volume and temperature (NVT ensemble). Non-bonding Van der Waals and electrostatic interaction energies were calculated using the Ewald summation method[5]. Typically, every 200th configuration was saved for analytical purposes. The simulation temperature was varied according to the purpose of the run.

Results and Discussion

Model preparation. The initial structure for the simulations was generated from a superlattice based on α-quartz using a procedure similar to that described by Kleestorfer *et al*[6]. A hexagonal periodic cell (a=49.10Å, b=49.10Å, c=5.402Å, α=90˚, β=90˚, γ=120˚) was created and used as the progenitor for all HMS models.

A series of HMS models, with varying pore diameter, were prepared by removing successive layers of Si and O atoms from the core of the superlattice. Si atoms with incomplete bonding configurations were fully saturated with hydroxy (OH) groups. The OH saturated models contained ~ 9 OH groups per nm^2 of internal surface. Model construction was, in each case, followed by geometry optimisation (energy minimization), equilibration and, then, a production MD run (100ps at 373K).

The models can be conveniently presented as *pseudo-2D* cross-sections due to the shallow thickness of the periodic cell in the c-direction (~5.4Å). Figure 1 illustrates one frame from an MD simulation of a fully hydrated mesopore that is 30Å in diameter.

Dehydration of fully hydrated mesopores. In Figure 1 adjacent OH pairs are connected by green lines. These mark the distance between the O of one OH group and the H of the adjacent OH group. When these atoms are close enough (<2.5Å) an H-bond is formed.

The circles surround OH group pairs that came closest in proximity during the first MD run at 373K. Their close proximity was deduced by plotting the 'length distribution' (frequency versus separation distance) for both of the two H-bonding atom pairs that are formed by adjacent OH groups. This plot is shown in Figure 2 for one adjacent pair. The plot shows that the adjacent H and O atoms are frequently close enough to form H-bonds and, hence it is assumed, in sufficient proximity for dehydration to occur.

Dehydration at the 6 circled locations by removal of water, leaving Si-O-Si linkages, reduced the surface silanol number from ~9 to ~7 OH/ nm^2.

Iterative replication of the procedure outlined above led to a series of partially dehydrated HMS models with silanol numbers in the range 2.5-7 OH/nm^2. For this purpose the molecular dynamic (MD) simulations were carried out at progressively higher temperatures (438, 498, 623 and 723K) chosen to correlate with the documented relationship between surface silanol concentration and pretreatment temperature for silica gel[7].

Preparing hybrid surfaces. When trimethoxyaminopropyl-silane is introduced into the mesopores, modeling results suggest that it spreads out over the surface, forming plenty of H-bonds (the blue dashed lines in Figure 3). It can be speculated that the formation of this 'surface film' may limit the number of silane molecules that can coordinate to and, hence, react with the surface OH groups. This may be one reason why tether loadings reported[8] for aminoalkylsilanes are not as high as would be expected if all surface silanols were accessible.

Hybrid material models were prepared by attachment of aminopropyl-silyl tethers to the surface, in a bidentate fashion, at silanol sites that provided the greatest (calculated) energy relief. The model illustrated in Figure 4 has 1.6 tethers per nm^2 and possesses a number of structural features (pore diameter, surface area, tether concentration) that are common to materials prepared in our laboratory[8].

It can also be seen that a number of the tethered aminogroups are still hugging the surface, a feature which is indicative of H-bonding interactions between the nitrogen (small blue circles) and the residual silanol groups.

Interactions with CO_2. Figure 4 also illustrates some of the interactions that may occur between the hybrid surface and gas-phase CO_2 when they are brought into proximity of each other. There is a clear tendency for CO_2 to form H-bonds - both with the tethered amine groups and with residual surface OH groups. The figure illustrates a situation where one CO_2 molecule (highlighted in yellow) becomes confined (on the MD timescale) in a structural pocket that might also be thought of as an 'energy-well'. It can be seen (Figure 5) that the mean square displacement versus time for this CO_2 molecule is substantially less than that for the average of all CO_2 molecules.

Conclusions

Visualisation and analysis of simulated molecular behaviour at the gas-solid interface offers fresh perspectives towards understanding the molecular interactions in these systems. This is enabling the development of improved synthetic strategies that will lead to improved CO_2 adsorption capacities.

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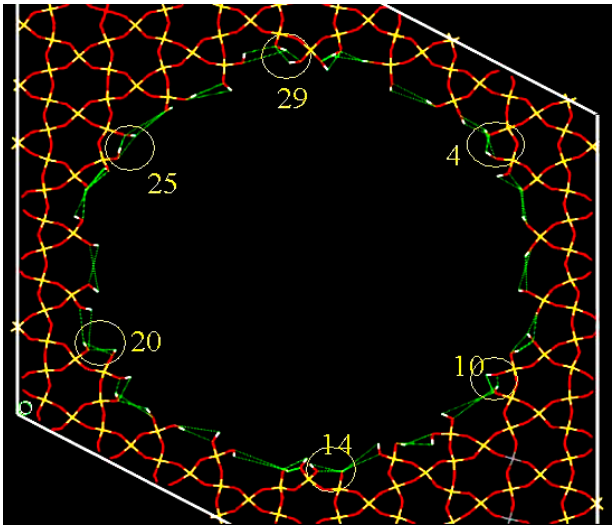

Figure 1. Cross-section of a fully hydroxylated 30Å diameter HMS mesopore.

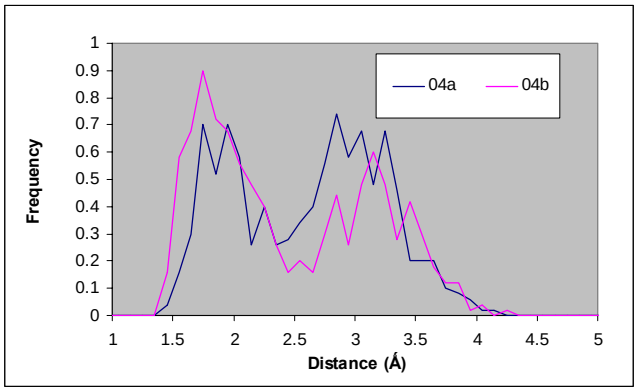

Figure 2. Length distribution for both H-bonds (a and b) that form across the hydroxy pair labeled 4 (refer Figure 1).

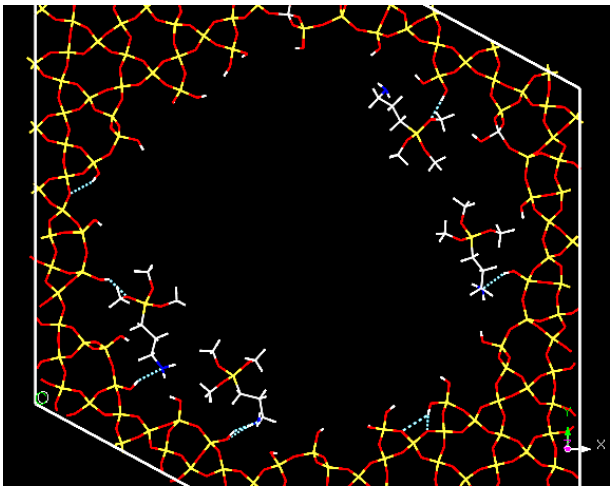

Figure 3. Molecular model illustrating H-bonding (blue-dashed lines) between trimethoxyaminopropylsilanes and a partially dehydrated (5 OH/nm^2) mesopore surface.

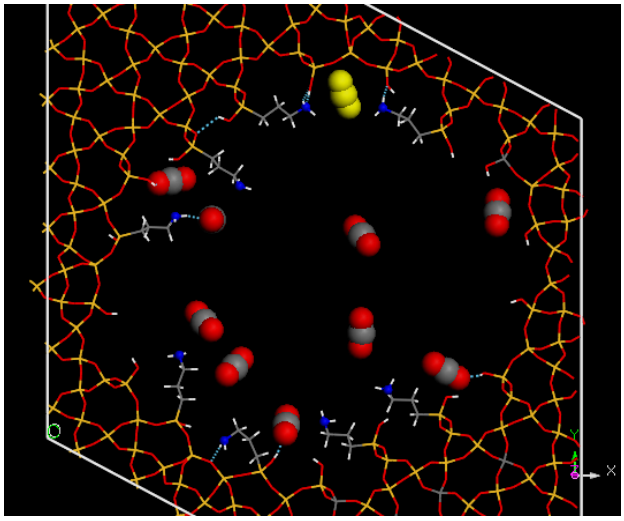

Figure 4. Molecular model illustrating H-bonding interactions between CO_2 molecules and the mesopore surface. The yellow CO_2 molecule appears to be confined by strong H-bonding.

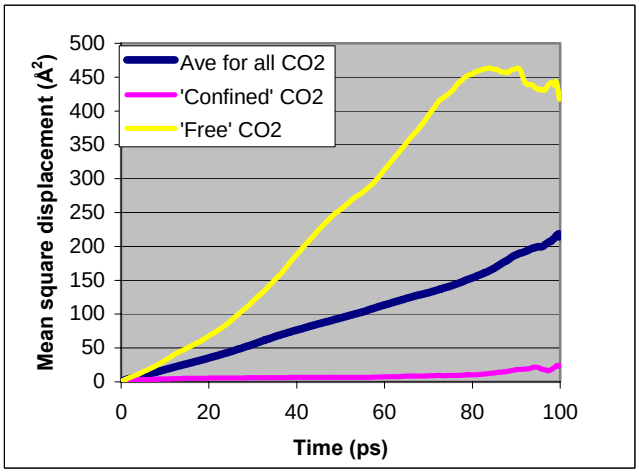

Figure 5. Mean square displacement characterizing (a) the average molecular motion of all CO_2 molecules and (b) the molecular motion of selected individual CO_2 molecules ('confined' and 'free'). Data correspond to the simulation illustrated by Figure 4.

References

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