Hydrogen adsorption and diffusion in amorphous, metal-decorated nanoporous silica

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ABSTRACT

Amorphous, nanoporous adsorbents composed of spherosilicate building blocks and incorporating isolated metal sites were investigated for their ability to adsorb and desorb hydrogen. This novel adsorbent contains cubic silicate building blocks (spherosilicate units: Si_8O_{20}), which are cross-linked by $SiCl_2O_2$ bridges and decorated with either $-OTiCl_3$ or $-OSiMe_3$ groups. The models for the structures were generated to describe experimentally synthesized materials, based on physical properties including density, surface area, and accessible volume. Adsorption isotherms and energies at 77 K and 300 K for pressures up to 100 bar were generated via molecular simulation describing physisorption only. The maximum gravimetric capacity of these materials is 5.8 wt% H_2, occurring at 77 K and 89.8 bar. A low density (high accessible volume) material with no $-OTiCl_3$ groups proved to be the best performing adsorbent. The presence of $-OTiCl_3$ did not enhance physisorption even on a volumetric basis, while the high molecular weight of Ti provided a strong penalty on a gravimetric basis. Pair correlation functions illustrate that the most favorable adsorption sites for hydrogen are located in front of the faces of the spherosilicate cubes. The self-diffusivity of hydrogen was reported and found to be highly correlated with accessible volume.

Introduction

Hydrogen is often proposed as a sustainable energy carrier [1–4], which can be produced from fossil fuels or from water couple with renewable sources of electricity [5–10]. However, its application, particularly in on-board vehicles, is limited by storage issues. Developing a reliable hydrogen storage system that meets the cost, safety, capacity and discharge rate requirements of the transportation sector is crucial. Methods for hydrogen storage include compressed gas, liquefaction, adsorption in metal hydrides, activated carbon, and metal organic frameworks (MOFs) [7,11]. The Department of Energy (DOE) sets the targets for onboard hydrogen storage systems

for light-duty vehicles for gravimetric capacity of 5.5 wt% hydrogen and volumetric capacity of 0.04 kg hydrogen/L to be achieved by 2017 [12]. These targets will allow some hydrogen-fueled vehicle platforms to meet customer performance expectations, while the "ultimate full fleet" targets of 7.5 wt% and 0.07 kg hydrogen/L are intended to facilitate the broad adoption of hydrogen-fueled propulsion systems.

A good storage media for hydrogen should perform both as an efficient adsorber and desorber, because it is not only the storage capacity that matters, but also the discharge rate. Hydrogen storage adsorbents that have been investigated so far either adsorb via chemisorption and display high capacities with slow discharge rates (e.g.: metal hydrides), or adsorb via physisorption with lower capacities but higher discharge rates (e.g.: single-walled carbon nanotubes (SWNTs) and MOFs) [13]. Neither category currently meets both the adsorptive and desorptive requirements effectively. In 1997, Bushnell et al. [14] performed quantum mechanical studies to identify the favorable binding energies for both adsorption and desorption of hydrogen in the structures with isolated Ti centers. Ti metal centers have binding energies that are between those associated with physisorption and chemisorption, making materials that incorporate them potentially interesting storage materials.

Motivated by this idea a synthetic strategy to make porous spherosilicate matrices that contain isolated titanium metal centers has been developed [15,16]. These materials have an inorganic cross-linked polymer-like structure with atomically dispersed Ti acting as isolated metal centers. In a reduced state, the Ti metal centers provide catalytic sites, which mimic those described by Bushnell et al. [14]. In an oxidized state, the Ti metal centers appear as $-OTiCl_3$, which still impacts the adsorption of H_2. In this study we computationally investigate the spherosilicate structures made up of polyhedral oligomeric silsesquioxane (POSS), which has the shape of a cube and the empirical chemical formula $(RSiO_{3/2})_8$ where R is either a functional ending group or a cross linker connecting it to another spherosilicate unit. POSS are part of a large family of polycyclic compounds consisting of silicon–oxygen bonds [17,18].

Metal-containing POSS compounds have been experimentally studied as metal catalyst supports [19]. Numerous elements throughout the periodic table have been incorporated successfully into POSS [15,16] opening paths to facilitate broad applications. Theoretical modeling of synthesis, assembly and properties for POSS systems have been previously investigated by McCabe et al. [20]. The adsorptive capability of POSS-based structures has been investigated in several studies. A Pd–POSS system has been analyzed by Maiti et al. [21] to investigate hydrogen catalysis and sequestration. They report density functional theory results on POSS binding energies at the Pd(110) surface, hydrogen storing ability of POSS and possible pathways of hydrogen radicals from the catalyst surface to unsaturated bonds away from the surface. Shanmugam et al. studied CO_2 adsorption [22], Xie et al. studied copper and nickel ions adsorption [23], Hongbo et al. studied N_2 adsorption [24], in different variations of POSS-based structures.

The family of cross-linked matrices of spherosilicate cubes used in this work has been prepared according to published procedures [15,16,19]. More details about experimental structures are included in our previous work on adsorption properties for methane and carbon dioxide in the same set of adsorbents [25]. Here we report the results of molecular-level simulations to study physisorption and diffusion of hydrogen in these materials, with the purpose of developing fundamental structure/property relationships. Particularly, we are interested in the impact of surface area (SA), accessible volume (AV) and $-OTiCl_3$ content on the adsorptive and diffusive behavior of H_2.

Simulation methods

Model for spherosilicate structures

Developing an atomistic model of an amorphous adsorbent is more challenging than for a crystalline material because in the latter case one can rely on atomic coordinates and unit cell parameters obtained from diffraction whereas in the former case, one must propose atomic coordinates and validate the resulting model through comparison to physical properties with those available from experiments (such as the chemical stoichiometry, pore size distribution, surface area, fraction of accessible volume and density of the material). In order to generate an atomistic structure for these amorphous, metal-decorated spherosilicate structures, we developed a multi-scale procedure which includes a mesoscale level modeling step followed by a molecular level modeling step. A detailed description of this procedure is included in our previous work [25]. Briefly, in the mesoscale level modeling step, four different coarse grain beads representing four different atomic groups were placed in a $50 \times 50 \times 50$ Å^3 cubic simulation box according to the relevant distances and angles between connected beads, so that the system agrees with the experimentally determined stoichiometry, density, surface area and accessible volume. The four groups are spherosilicate cubes (Fig. 1(a)), O_2SiCl_2 connecting bridges (Fig. 1(b)) and two groups that terminally binds to the vertices of the spherosilicate cubes: $-OTiCl_3$ (Fig. 1(c)) and $-OSi(CH_3)_3$ (trimethylsilyl or $-OSiMe_3$) (Fig. 1(d)). A mesoscale level energy minimization in which the coarse grain beads were translated was performed using canonical Monte Carlo simulation to avoid overlap between the beads and to obtain a stable structure. In the molecular level modeling step the coarse grain beads were replaced with their relevant atomic descriptions and rotated to obtain the correct orientation using the downhill simplex method [26]. Fig. 1(e) and (f) illustrates a coarse grain structure and an atomistic structure respectively.

Using this procedure we modeled nine materials for this study, by varying two physical properties at three levels. The first property is density of the adsorbent. Of course, a change in density corresponds to a change in the fraction of accessible volume in the adsorbent as well as a commensurate change in surface area. The second property is $-OTiCl_3$ content. As noted above there are two types of non-connecting end groups attached to the vertices of the spherosilicate cube, $-OTiCl_3$ and $-OSi(CH_3)_3$. Values of 0%, 50% and 100% Ti correspond to the fraction of end groups which were $-OTiCl_3$. For each level of $-OTiCl_3$ content, there are three levels of material density,