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Microporous and Mesoporous Materials

Effect of organic groups on hydrogen adsorption properties of periodic mesoporous organosilicas

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ABSTRACT

We investigate the hydrogen adsorption properties of periodic mesoporous organosilicas (PMOs) and focus, in particular, on how these properties are affected by diverse organic groups embedded in the walls. PMOs with π electrons on the pore surface adsorb more hydrogen molecules per unit area and have a higher isosteric heat of hydrogen adsorption (Q_{st}). The number of adsorbed hydrogen molecules per unit area correlates well with the density of organic groups on the pore surface. We attribute the high Q_{st} to the high polarizability of organic groups with π electrons, which enhances the dispersion force. The molecular order of organic groups affects the adsorption-site affinity to hydrogen molecules as well as the location of adsorption sites. For phenylene-bridged PMOs with crystal-like pore walls, Q_{st} decreases rapidly with increasing hydrogen loading, which indicates two types of adsorption sites with different affinities to hydrogen molecules: one is an exposed CH bond and the other is a siloxane bond. However, Q_{st} for phenylene-bridged PMOs with amorphous pore walls exhibits a moderate slope, which might be caused by the random order of organic groups; this results in several types of adsorption sites with various affinities.

1. Introduction

Periodic mesoporous organosilicas (PMOs) are a new class of porous inorganic–organic hybrid materials that are synthesized by surfactant-directed self-assembly of various organosilane precursors with bridging organic groups. PMOs show great potential as adsorbents, catalysts, and photoactive materials because of their versatile surface chemistry incorporated with a high surface area and uniform pore-size distribution [1,2]. Porous materials such as PMOs are expected to be suitable as hydrogen storage materials, which would be significant because hydrogen is seen as a possible clean energy source for a carbon-free society.

The distribution of organic groups on the pore surface of PMOs is relatively homogeneous compared with the organically functionalized mesoporous silica modified by post-grafting with organosilanes. Furthermore, the use of organosilanes with aromatic groups enables the fabrication of a molecularly ordered framework as a result of hydrophobic and hydrophilic interactions that direct the self-assembly of organic linkers with a lamellar arrangement in the wall [3,4].

The organic groups on the surface of PMOs induce specific interactions, which are advantageous for adsorption and/or separation. In particular, the surface chemistry of phenylene-bridged PMO

with crystal-like pore walls (CW-Ph-PMO) [3] has been widely investigated [5–8]. Onida et al. investigated the interaction between the surface of CW-Ph-PMO and various probe molecules by using variable-temperature Fourier transform-infrared spectroscopy [5–7]. CW-Ph-PMO consists of ordered isolated silanols and phenylene rings on the surface; the former act as Lewis-acid sites, which are weaker than the isolated silanols on pure silica, and the latter exhibit the features of Lewis-base sites [5]. Dual surface functionality, such as that due to phenylene groups and silanol groups, induces a double interaction that enables strong adsorption of certain probe molecules. In addition, the surface of CW-Ph-PMO is more polarizable than that of mesoporous silica owing to the phenylene groups, which provide high electron density; thus, the dispersion force is enhanced [6,7]. Comotti et al. reported that, compared with cyclohexane, the aromatic molecules benzene and hexafluorobenzene with π electrons and CW-Ph-PMO exhibit a steeper adsorption isotherm at low surface coverage [8]. The phenylene rings embedded perpendicular to the pore walls of CW-Ph-PMO and exposing polarizable CH bonds on the surface interact with guest aromatic molecules by favorable weak CH_{host}–π_{guest} interactions. On the other hand, the molecular order of aromatic rings in the walls may influence the adsorption properties. The phenylene-bridged PMO with amorphous pore walls (AW-Ph-PMO) consists of slightly more acidic silanols compared with CW-Ph-PMO [9]. Iodine adsorption measurements of CW-Ph-PMO and AW-Ph-PMOs reveal that, compared with the surface of

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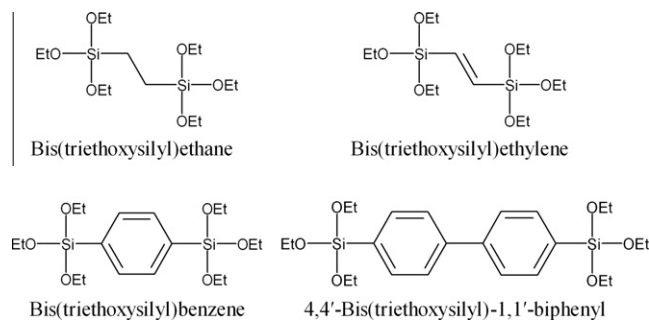*E-mail address:* okubo@chemsys.t.u-tokyo.ac.jp (T. Okubo).

Fig. 1. Organosilanes used in this study.

crystal walls, the surface of amorphous walls have more exposed phenylene sites, which can strongly interact with iodine [10].

The capability of PMOs to adsorb gas increases with more polarizable surface. For example, CW-Ph-PMO adsorbs methane remarkably well; up to 4 wt.% at 195 K and 700 Torr, which exceeds the capability of zeolites containing one dimensional channels [8]. Jung et al. reported that, at 77 K and at room temperature, CW-Ph-PMO adsorb hydrogen at a rate higher than that of mesoporous silica [11]. On the basis of a quantum calculation, they suggested that this enhanced hydrogen uptake is due to the phenylene groups on the surface of CW-Ph-PMO. However, the effects of diverse embedded organic groups and their molecular order on the hydrogen adsorption properties of PMOs are currently not well understood.

Hydrogen uptake on porous materials at ambient temperature is limited because of the weak interaction between the surfaces of porous materials and hydrogen molecules. To overcome this limitation, the interaction should be enhanced. Previous studies suggested that introducing additional adsorption sites with high affinity to hydrogen molecules onto the pore surface can enhance hydrogen uptake [12–14]. We have shown that lithium doping into mesoporous silica can enhance hydrogen uptake and the isosteric heat of adsorption [13,14]. Simultaneously, understanding the interaction between the surfaces of porous materials and hydrogen molecules is a key for properly designing pore surfaces. Recently, various organic groups have been introduced into not only PMOs but also metal–organic frameworks [15], covalent organic frameworks [16], and conjugated microporous polymers [17,18], all of which have potential for hydrogen storage. The diverse organic groups embedded in PMOs can serve as suitable models for studying the interaction between these groups and hydrogen molecules.

In this paper, we focus on the effects of diverse embedded organic groups and their molecular order on the hydrogen adsorption properties of PMOs. Five types of PMOs with two-dimensional hexagonal structures were synthesized from organosilane precursors (Fig. 1). To understand the interactions, we studied the number of adsorbed hydrogen molecules per unit area and the isosteric heat of hydrogen adsorption.

2. Experimental

Ethylene-bridged PMO (E-PMO), vinylene-bridged PMO (V-PMO), CW-Ph-PMO, AW-Ph-PMO, and biphenylene-bridged PMO with crystal-like walls (CW-Biph-PMO) were synthesized by following previous studies [3,4,19–21]. For comparison, pure mesoporous silica (MPS) was also synthesized [22]. These materials were characterized by the following measurements. X-ray diffraction (XRD) was performed using an M03X–HF22 (Mac Science) equipped with a CuKα radiation source (wavelength 1.5406 Å). Nitrogen adsorption/desorption and hydrogen adsorption measurements were performed at 77 and 87 K by using an

AUTOSORB-1-MP (Quantachrome Instruments). The specific surface area of the samples was calculated from the adsorption isotherm of nitrogen by the Brunauer–Emmett–Teller (BET) method. The pore-size distribution was determined from the adsorption isotherm of nitrogen at 77 K by the Barret–Joyner–Halenda (BJH) method. The isosteric heat of hydrogen adsorption (Q_{st}) was calculated via a virial equation, which gives reliable Q_{st} [23]. The following virial-type expansion with temperature-independent parameters a_i and b_i was applied:

$$\ln P = \ln N + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i$$

where P represents pressure, N is the amount adsorbed, T is the absolute temperature, and m and n are the number of coefficients required to adequately describe the isotherms. From these results, Q_{st} is calculated as follows:

$$Q_{st} = -R\sum_{i=o}^{m} a_i N^i,$$

where R is the universal gas constant.

3. Results and discussion

3.1. Structural characterization

XRD patterns of the samples are shown in Fig. 2. All samples exhibit peaks in the low-angle region, indicating the presence of long-range order. The corresponding d values are listed in Table
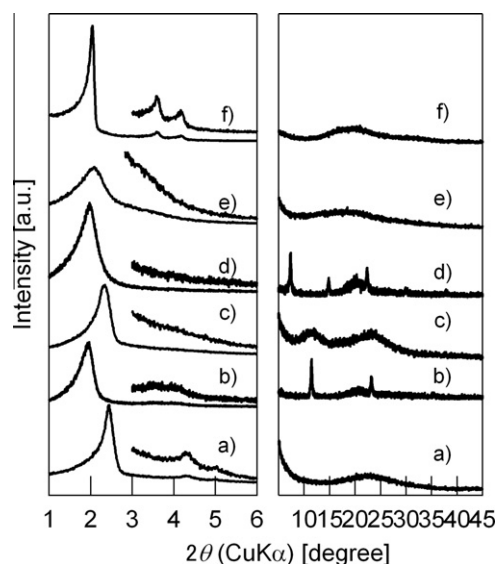

Fig. 2. Powder XRD patterns for (a) MPS, (b) CW-Ph-PMO, (c) AW-Ph-PMO, (d) CW-Biph-PMO, (e) E-PMO, and (f) V-PMO.

Table 1
Structural parameters of the samples used in this study.

Sample	d value (nm)	Surface area (m²/g)	Pore volume (cc/g)	Pore size (BJH) (nm)
MPS	3.6	1302	0.88	2.2
CW-Ph-PMO	4.5	730	0.55	2.3
AW-Ph-PMO	3.8	1365	0.80	1.9
CW-Biph-PMO	4.5	744	0.44	1.9
E-PMO	4.2	1347	0.91	2.2
V-PMO	4.3	842	1.09	2.7