Pillared carbons consisting of silsesquioxane bridged graphene layers for hydrogen storage materials

Yoshiaki Matsuoa,*, Sakae Uedaa, Kentaro Konishi, Juan Pablo Marco-Lozar, Dolores Lozano-Castellob, Diego Cazorla-Amorós

aDepartment of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, 2167 Shoshia Himeji, Hyogo 671-2280, Japan
bMaterials Institute, University of Alicante, Apdo. 99, Carretera Sant Vicent del Raspeig, Alicante 03690, Spain

ARTICLE INFO

Article history:
Received 6 February 2012
Received in revised form 6 April 2012
Accepted 7 April 2012
Available online 5 May 2012

Keywords:
Pillared carbon
Hydrogen storage
Silylated graphite oxide
Heat of adsorption

ABSTRACT

Various pillared carbons consisting of silsesquioxane bridged graphene layers were prepared from the pyrolysis of silylated graphite oxides. Pillared carbons with interlayer spacings of 1.34–1.6 nm were obtained when prepared from graphite oxide silylated with alkyltrichlorosilane and then with methyltrichlorosilane. The graphene layers of pillared carbons were not well ordered when it was obtained from graphite oxide silylated with 3-aminopropyltriethoxysilane. The hydrogen excess adsorption of pillared carbons at ambient temperature reached 0.6 wt% and showed relatively high total hydrogen storage of 14 g/L at 20 MPa. Moreover, pillared carbon obtained from graphite oxide repeatedly silylated with methyltrichlorosilane showed a high adsorption heat of 8–11 kJ/mol.

1. Introduction

Among the hydrogen storage technologies, physisorption by nanostructured materials such as porous coordination polymers/metal organic frameworks (PCP/MOF) or porous carbon based materials are attracting much attention due to their tunable pore structure, fast kinetics, light weight, chemical stability, etc. [1,2]. However, it is still difficult to reach the US Department of Energy (DOE) targets for on-board hydrogen storage systems: 6.0 wt% and 45 g/L by the year 2010, and 9.0 wt% and 81 g/L by 2015 [3]. Their generally accepted hydrogen storage capacities at ambient temperatures and applicable pressure are less than 3 wt%. Moreover, they are suffering from small isosteric heat of adsorption of hydrogen, which is an indication of the strength of the interaction between hydrogen. It should be around 15 kJ/mol for hydrogen storage at ambient temperatures [4]. The high surface areas either per unit mass or per unit volumes are primarily desirable for high uptake of hydrogen and the high pore volume and appropriate pore sizes are also important because the strength of adsorbent/guest interactions is enhanced when the pore size becomes smaller. The isosteric heat of adsorption of hydrogen and adsorbents is usually in the range of 4–8 and 3.5–6.5 kJ/mol for carbons and PCP/MOF, respectively. In case of PCP/MOF materials, in order to achieve high heat of adsorption values, unsaturated metal sites are usually needed [5–7]. In this sense, carbon materials without heavier metals seem attractive if high heat of adsorption is achieved, though the hydrogen storage capacities at ambient temperatures and high pressures are still low values of around 2% [8,9]. Moreover, for carbon based materials, the hydrogen gas heat of adsorption exceeding 8 kJ/mol (up to 11 kJ/mol) has been

*Corresponding author. Tel./fax: +81 792674898.
E-mail address: ymatsu@eng.u-hyogo.ac.jp (Y. Matsu).
reported only for that prepared from the chlorination of titanium carbide at 800 °C at the low loading regions [10]. Theoretical calculation has predicted that the slit type pores consisting of two expanded graphene layers with the width of around 0.6 nm show high isosteric heat of adsorption of hydrogen of 15 kJ/mol and are suitable for hydrogen storage materials [4,11,12]. However, it seems very difficult to realize expanded graphene layers without any supports inserted between them. Therefore, pillaring of graphene or graphite oxide (recently called graphene oxide) with carbon nanotube fragments or benzenediboronic acids have been considered and theoretical calculations have predicted that the resulting materials show high hydrogen storage capacities [13–15]. In fact, Burress et al. provided a high isosteric heat of adsorption of hydrogen for graphite oxide framework materials in which graphite oxide layers are connected by benzenediboronic acid pillars, though the amount of hydrogen stored was low even at low temperatures [14]. In this context, we have recently prepared microporous pillared carbons from the pyrolysis of silylated graphite oxide in which adjacent graphene layers are connected with silica or silsesquioxane based pillars and the calculated pore widths of them are very small (~0.7 nm) [16–19]. Moreover, the distance between two adjacent pillars is well controlled between 0.36 and 0.40 nm, based on the inclusion behavior of polar organic molecules with various molecular weights [20,21]. Preparation of pillared carbons from the pyrolysis of intercalation compounds of graphite oxide have been reported by several researches, however, no XRD peak indicating the layered structure was observed in the resulting materials [22–26]. On the other hand, our pillared carbons showed several (002) XRD peaks and possess more ordered layered structure [16–21]. A typical structure of pillared carbon consisting of silsesquioxane bridged graphene prepared from the pyrolysis of graphite oxide silylated with methyltrichlorosilane is shown in Fig. 1 [20]. The pores in pillared carbon are surrounded by both pillars and hydrophobic carbon layers, therefore, hydrogen molecules are expected to be well stabilized in them and pillared carbons are suitable for the storage of hydrogen gas. The use of different silylating reagents for the silylation of graphite oxide can change the functional groups in the pillars or the structure of them, which would modify the size or nature of pores of pillared carbons. For example, organic groups except for methyl ones in them are removed during heating at 500 °C or higher, therefore, they are replaced by hydroxyl groups in the resulting pillars. The addition of long alkyl chains instead of methyl groups in the silylated graphite oxide can hinder some of the reaction sites for silylation, leading to the formation of defects in the silsesquioxane pillars. In this study, the hydrogen adsorption properties of various pillared carbons have been investigated and high isosteric heat of adsorption of hydrogen observed for one of them is reported.

2. Experimental

Preparation of pillared carbon was performed in the same manner as reported in our previous studies [18–21]. Graphite oxide (abbreviated as GO) was prepared based on the Brodie’s method [27] and oxidation procedure was repeated five times. The composition of the resulting GO was C_{6}H_{12}O_{4.5} (formula weight: 179). GO (100 mg) was mixed with n-butylamine (C_{6}H_{13}NH_{2}, hereafter abbreviated as C_{6}A, 2 mL; 32 mol per GO unit of C_{6}H_{12}O_{4.5}) as an exfoliating reagent in a sealed glass vial under an Argon atmosphere and the resulting solution was sonicated, then heated at 60 °C for 1 h. Dry toluene (5 mL, water content<30 ppm) was added to this solution and the solution was again sonicated. Silylating reagent (methyltrichlorosilane, CH_{3}SiCl_{3}: 0.90 mL, octyltrichlorosilane, C_{8}H_{17}SiCl_{3}: 1.75 mL, decyltrichlorosilane, C_{10}H_{21}SiCl_{3}: 2.01 mL, tetradecyltrichlorosilane, C_{14}H_{29}SiCl_{3}: 2.50 mL, octadecyltrichlorosilane, C_{18}H_{37}SiCl_{3}: 3.01 mL; these amounts correspond to 13 mol per GO unit of C_{6}H_{12}O_{4.5}) was added to the resulting and then allowed to stand for 2 day at 60 °C. Hereafter the silylating reagents are abbreviated as C_{3}Si, C_{8}Si, C_{10}Si, C_{14}Si and C_{18}Si, respectively. After centrifugation at 4000 rpm for 20 min, the precipitate was washed with dry toluene, ethanol and finally acetone. The obtained silylated GO samples were silylated with C_{3}Si in the same manner as described above or with 3-aminopropyltriethoxysilane (abbreviated as APS) in toluene at 80 °C for 1 day. The silylation of GO silylated with C_{3}Si and silylating reagents with longer alkyl chain lengths was repeated for 2 and 3 times, respectively. The samples are denoted as C_{3}SiGO-C_{6}Si (n = 1, 8 and 10). In case of the silylation of C_{3}SiGO with APS by a two-step method [19], the samples were put in toluene (20mL) and APS (1 mL) was added. The mixture was heated at 90 °C for 2 days. Then, it was centrifuged and the precipitate was washed with acetone and ethanol. The resulting samples were denoted as C_{3}SiGO-APS (n = 8, 14 and 18). The compositions of these samples were determined as above, assuming that the ethoxy groups in APS were converted to hydroxyl groups.

The resulting silylated GO was thermally reduced at 500 and 600 °C under dynamic vacuum to convert GO to graphene. The temperature increase rate was 1 °C min^{-1} and the amount of the sample was less than 200 mg in order to avoid the deflagration of GO layers due to the heat generated during the removal oxygen from GO layers. The obtained pillared carbons are denoted as C_{n}SiGO-C_{3}Si(T) or C_{n}SiGO-APS(T) in which “T” in parenthesis means the temperature for pyrolysis. When long alkyl chains or 3-aminopropyl groups are included in the precursors, they are removed during pyrolysis and would be compensated by some oxygen containing functional groups such as hydroxyl ones. As the result, it is expected that the structure and properties of the pillars, accordingly the nature of the pores is modified. The silicon content was estimated from the weight of residual SiO_{2} after thermogravimetric measurement. These samples were analyzed by X-ray diffraction (Rigaku, Rint-2100, CuKα), thermogravimetry (TG; Shimadzu, TGA-50), and nitrogen adsorption (Bel Japan Inc., BELSORP-max, –196 °C) measurements. TG measurement was performed under air with the temperature increase rate of 5 °C/min between room temperature and 800 °C. The silicon content of silylated GO and pillared carbon was determined from the weight of residual SiO_{2} after thermogravimetric analysis. The packing density of these materials was determined by pressing a given amount of sample (in the range of 0.5–0.2 g) in a mould with a cross-sectional area of 1.31 cm² and a load of 1000 kg and using a cylindrical rod for pressing. The
measurement of the height of the rod with the mould empty and with sample, after pressing and releasing the applied load, permits the evaluation of the volume of the material and, then, the packing density. The difference of heights obtained varied from 0.38 to 0.19 cm. The measurements were repeated several times. The densities obtained have an error smaller than 3%.

Hydrogen adsorption measurements were carried out at 25, 50 and 75 °C and at high pressures, as reported in the previous literature [28]. Hydrogen isotherms were obtained in an automatic volumetric apparatus designed and built up in our laboratory to perform hydrogen isotherms up to 20 MPa. The manifold of the apparatus was kept at 35 ± 0.1 °C. Also, the sample cell was refrigerated at 25 ± 0.1 °C, by means of a liquid bath. Manifold volume was calibrated with a standard volume, carrying out helium isotherms. In order to assure that the apparatus was leak-free, hydrogen leak test was executed at 9 and 15 MPa during 28 h, the leak rate resulted below 10⁻⁶/s. The bulk gas amounts have been calculated by the equation of state of Modified-Benedic-Webb-Rubin [29], and the cell volume has been calculated taken into account the correction described in the literature [30]. Prior to the adsorption measurement, the sample was degassed at 250 °C during 4 h under vacuum. After that, the sample was located in the sample holder, and then evacuated at 130 °C during 4 h in vacuum. Sample weight was about 700 mg. Hydrogen and helium gases used in the experiments were 99.9995% pure. As a reference, the hydrogen adsorption behavior of commercial available zeolite, ZSM-5 with a pore diameter of 0.54 nm was also investigated. The BET surface area, micropore volume determined from the adsorption data of N₂ and CO₂ were 371 m²/g, 0.19 and 0.13 mL/g, respectively.

3. Results and discussion

3.1. Preparation and characterization of pillared carbons

Fig. 2A shows the X-ray diffraction patterns of pillared carbons prepared at 500 °C from C₆SiGO–C₆Si. The diffraction
peak at 2q = 13.76 and 20.78° are indexed as (002) and (003), respectively and the interlayer spacing was calculated to be 1.34 nm as shown in our previous paper [20]. When GO samples silylated with silylating reagents having longer alkyl chain lengths were used as starting materials, the interlayer spacing slightly increased to 1.41 and 1.43 nm (Fig. 2C and E). At higher temperature of 600°C, the diffraction peaks considerably shifted to lower angle and became broader, and the interlayer spacing slightly increased to 1.47 and 1.6 nm, respectively (Fig. 2B and D). On the other hand, the diffraction peaks observed for the samples obtained from GO silylated by a two-step method using APS were broader and the interlayer spacing was not determined (Fig. 2F).

Table 1 – Porous texture parameters deduced from the N2 and CO2 adsorption isotherms at −196 and 0°C, respectively, for various pillared carbons.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Temp./°C</th>
<th>L/nm</th>
<th>S BET/m²/g</th>
<th>V w (DR, CO₂)/mL/g</th>
<th>V w (N₂)/mL/g</th>
<th>Si content/%</th>
<th>Packing density/g/mL</th>
<th>He density/g/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₈SiGO-C₈Si</td>
<td>500</td>
<td>1.34</td>
<td>562</td>
<td>0.29</td>
<td>0.21</td>
<td>21.9</td>
<td>0.8</td>
<td>2.1</td>
</tr>
<tr>
<td>C₈SiGO-C₁₀Si</td>
<td>600</td>
<td>1.43</td>
<td>591</td>
<td>0.27</td>
<td>0.15</td>
<td>21.3</td>
<td>0.52</td>
<td>1.92</td>
</tr>
<tr>
<td>C₁₀SiGO-C₈Si</td>
<td>500</td>
<td>1.41</td>
<td>839</td>
<td>0.38</td>
<td>0.22</td>
<td>21.3</td>
<td>0.7</td>
<td>2.1</td>
</tr>
<tr>
<td>C₁₀SiGO-C₁₀Si</td>
<td>600</td>
<td>1.6</td>
<td>942</td>
<td>0.42</td>
<td>0.15</td>
<td>20.8</td>
<td>0.55</td>
<td>2.10</td>
</tr>
<tr>
<td>C₁₀SiGO-APS</td>
<td>500</td>
<td>*</td>
<td>652</td>
<td>0.26</td>
<td>0.17</td>
<td>40.6</td>
<td>0.50</td>
<td>1.92</td>
</tr>
<tr>
<td>C₈SiGO-APS</td>
<td>500</td>
<td>*</td>
<td>675</td>
<td>0.22</td>
<td>0.17</td>
<td>25.6</td>
<td>0.6</td>
<td>2.1</td>
</tr>
<tr>
<td>C₁₀SiGO-APS</td>
<td>500</td>
<td>*</td>
<td>675</td>
<td>0.22</td>
<td>0.17</td>
<td>25.6</td>
<td>0.6</td>
<td>2.1</td>
</tr>
</tbody>
</table>

3.2. Hydrogen storage in pillared carbons

Fig. 3 shows the N₂ adsorption isotherms at −196°C of pillared carbons obtained above. The isotherms are basically classified to type 1 and the samples were microporous. The amount of the adsorbed N₂ was unchanged during desorption for the pillared carbon of C₁₀SiGO-C₈Si(500). This indicates that it was difficult to reach equilibrium because of the difficulty in the diffusion of N₂ molecules and the distance between adjacent pillars was very small as suggested by the inclusion behavior of organic molecules reported in our previous study. When the alkyl chain length in the precursor or heat treatment temperature increased, the BET surface area of the resulting pillared carbon increased except for C₈SiGO-C₁₀Si(500) and reached 942 m²/g for C₈SiGO-C₈Si(600) (Table 1). On the other hand, pillared carbons prepared from C₈SiGO-APS were almost identical, independent of the alkyl chain lengths in the precursors and the BET surface area was in the range of 652–675 m²/g. The properties of the pillared carbons prepared from various silylated graphite oxide precursors are summarized in Table 1. Here, note that the packing density of some of the pillared carbons reached 0.8 g/mL, which was almost twice of the activated carbon with high surface area.

Fig. 4 shows the hydrogen excess adsorption isotherms for various pillared carbons at 25°C, together with that of ZSM-5 zeolite. The isotherms for pillared carbons include the error bars for each datum point to show the reliability of the experiments. The amount of adsorbed hydrogen on ZSM-5 zeolite increased in a similar manner to those on pillared carbons at lower pressure, however, it became lower at higher pressures than 10 MPa. In case of the pillared carbons prepared from C₈SiGO-C₈Si, the adsorbed amount of H₂ increased with decreasing in the alkyl chain length in the precursors (Fig. 4a) and increasing in the heat treatment temperature (Fig. 4c). The amount of hydrogen adsorbed at 20 MPa reached 0.58 wt% for C₈SiGO-C₈Si(600). On the other hand, in case of the pillared carbon prepared by a two-step method using APS, C₈SiGO-APS(500) gave a largest value of 0.6 wt% at 20 MPa (Fig. 4b). It has been shown that a linear trend is observed for the amount of the hydrogen adsorbed (weight percent) at 20 MPa and 25°C for various carbons versus the total micropore volume estimated from the CO₂ adsorption at 0°C (V m(CO₂)) [30].

Fig. 5 shows the relationship
between $V_{mp}(\text{CO}_2)$ and the amount of hydrogen adsorbed at 20 MPa on pillared carbons, together with those of ZSM-5, carbon nanotube and activated carbons mentioned above. The adsorbed amounts of hydrogen on pillared carbons were higher than those expected from the linear trend observed for activated carbons and carbon nanotubes, while that of ZSM-5 showed a good correlation. Moreover, interestingly, the adsorbed hydrogen on pillared carbons was not always large for those with larger $V_{mp}(\text{CO}_2)$. Note that, no good correlation with the adsorbed amount of hydrogen was obtained for the micropore volume estimated from the $a$ plot, ordered stacking structure nor BET surface area. At this moment, it is difficult to know the reason for this behavior, however, our tentative explanations are as follows. Pillared carbons possess small pores available only for small hydrogen molecules and/or flexible pillars in pillared carbons allowed to create additional pores for hydrogen molecules during adsorption of

**Fig. 4** – Hydrogen excess adsorption isotherms of various pillared carbons.

![Graph](image)

**Fig. 5** – Relationship between narrow micropore volume and hydrogen excess adsorption capacity on pillared carbons, together with those of +, zeolite (ZSM-5), □, activated carbons; and Δ, carbon nanotubes.

between $V_{mp}(\text{CO}_2)$ and the amount of hydrogen adsorbed at 20 MPa on pillared carbons, together with those of ZSM-5, carbon nanotube and activated carbons mentioned above. The adsorbed amounts of hydrogen on pillared carbons were higher than those expected from the linear trend observed for activated carbons and carbon nanotubes, while that of ZSM-5 showed a good correlation. Moreover, interestingly, the adsorbed hydrogen on pillared carbons was not always large for those with larger $V_{mp}(\text{CO}_2)$. Note that, no good correlation with the adsorbed amount of hydrogen was obtained for the micropore volume estimated from the $a$ plot, ordered stacking structure nor BET surface area. At this moment, it is difficult to know the reason for this behavior, however, our tentative explanations are as follows. Pillared carbons possess small pores available only for small hydrogen molecules and/or flexible pillars in pillared carbons allowed to create additional pores for hydrogen molecules during adsorption of

**Fig. 6** – Hydrogen excess adsorption isotherms on (a) C$_n$SiGO–C$_1$Si(500) and (b) C$_n$SiGO–C$_1$Si(600). The measurements were performed at ●, 25, ▲, 50 and ■, 75 °C.
them. Fig. 6 shows the excess adsorption isotherms for hydrogen on pillared carbon obtained from C1SiGO-C1Si(500) and C1SiGO-C1Si(600) measured at 25, 50 and 75 °C up to 20 MPa. In both cases, the adsorbed hydrogen decreased with increasing in the adsorption temperature since hydrogen storage is based on the physisorption. Fig. 7 shows the isosteric heat of adsorption calculated based on the data in Fig. 6 by using the Clausius–Clapeyron equation [31]. The heat of adsorption observed for C1SiGO-C1Si(600) with less ordered structure was around 5.2 kJ/mol and slightly decreased with increasing in the H2 uptake which is commonly observed for other carbon materials. On the other hand, it was 8 kJ/mol at lower H2 uptake and increased to 11 kJ/mol for C1SiGO-C1Si(500), which was higher than those observed for the other materials. The pores of pillared carbon are surrounded both by carbon layers and pillars consisting of silicon, oxygen and methyl groups. The carbon layers are separated by a relatively large distance of 1.34 nm. On the other hand, that between adjacent pillars is estimated to be 0.36–0.4 nm based on the inclusion behavior of polar organic molecules [20] and small pore width of 0.45 nm estimated from HK method [21]. The pore structure is not fully understood yet, however, in such pores, hydrogen molecules are expected to be greatly stabilized, which is responsible for the high adsorption heat. The increase in the heat of adsorption at higher loading of hydrogen is also unusual. Based on our previous results on the reversible intercalation behavior of the organic molecules into pillared carbons, the pillars between carbon layers are quite flexible [21]. Though it is difficult to predict the intercalation behavior of molecules under high pressure, the interlayer expansion is not expected upon adsorption of hydrogen molecules, considering the small change in the interlayer spacing upon intercalation of smaller organic molecules. In such a case, the space available for the adsorption of hydrogen molecules becomes smaller and accordingly hydrogen molecules are more stabilized. On the other hand, in case of C1SiGO-C1Si(600) with a less ordered stacking structure, hydrogen molecules are not well stabilized in pillared carbons because of the decreased density of pillars as estimated from the larger interlayer spacing and similar Si content. From the application point of view, total storage capacity in a given size of container is important. Fig. 8 shows the total storage capacity in a 1 L container which was estimated based on the adsorbed and compressed hydrogen, the packing and helium densities, together with adsorbed hydrogen per volume. While

Fig. 7 — Heat of adsorption for • C1SiGO-C1Si(500) and ○ C1SiGO-C1Si(600).

Fig. 8 — Total hydrogen storage capacity of various pillared carbons on the basis of a 1 L container (filled marks), together with the adsorption excess data (open marks).
the adsorbed hydrogen was 2–4 g/L, total storage capacity was in the range of 12–14 g/L, which was slightly smaller than that observed for activated carbons or zeolite templated carbon with much higher surface areas (less than 20 g/L) [9,23]. This is ascribed to the high packing density of the present pillared carbons.

4. Conclusion

In summary, the hydrogen adsorption excess capacity of pillared carbon at ambient temperature reached 0.6 wt% and relatively high total hydrogen storage of 14 g/L was obtained at 20 MPa, moreover, one of the pillared carbons with a higher ordered stacking structure showed high adsorption heat. At this moment the hydrogen storage capacity on pillared carbons was still smaller than the target values, however, further increase would be expected by controlling the pore structures of them.

Acknowledgement

The authors gratefully acknowledge the financial supports from Canon foundation, MICINN (project CTQ2009-10813), Generalitat Valenciana and FEDER (PROMETEO/2009/047).

REFERENCES