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Preparation of microporous pillared carbons from the silylated graphite oxide prepared by a two-step method

Yoshiaki Matsuo*, Takeshi Komiya, Yoshiohiro Sugie

Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, 2167 Shosha Himeji, Hyogo 671-2201, Japan

1. Introduction

Porous carbons are attracting much attention for the support of catalysts, gas storage, adsorbents, electrode of electric double layer capacitor, etc. Activated carbons are typically used for these purposes; however, it is difficult to control the size and distribution of pores by the conventional surface activation processes. Therefore, various synthetic techniques have been introduced to obtain porous carbons, such as template method [1–5], selective elimination of specific elements or functional groups from ceramics [6,7] or polymers [8,9] and so on. In this context, we have prepared pillared carbons by pyrolysis of silylated graphite oxide in which the adjacent carbon layers are connected with each other by silica or silsesquioxane pillars containing methyl groups through C–O–Si bondings [10–12]. The structure of this type of pillared carbon was quite different from that of the other porous carbons prepared from the intercalation compounds of graphite oxide [12–18]. In these cases, the intercalated species were removed from the layers during the thermal reduction process of graphite oxide to carbon because of the weaker interaction between graphite oxide layer and intercalated species and, therefore, composite materials of carbon/silica or iron oxide were formed. It was expected that our pillared carbons possess micropores surrounded by pillars and carbon layers and high surface area; however, the BET surface area of them was less than 240 m²/g. Our previous results suggested that this was due to the narrow space between pillars for nitrogen molecules to pass [12]. More recently, we have succeeded to create micropores in pillared carbons and the BET surface area reached 550 m²/g; however, the distance between pillars were less than 0.4 nm and the diffusion of nitrogen molecules are still difficult [19].

In order to increase the surface area and to create more pores in pillared carbons, it would be necessary to reduce the lateral size of the pillars, for example, by replacing methyl groups in the pillars with relatively smaller functional groups such as hydroxyl groups or introducing defects into them. In this study, pillared carbons with a higher surface area were prepared by the pyrolysis of graphite oxides silylated with two different silylating reagents without methyl groups. As reported in our previous paper [12], heat treatment of graphite oxide repeatedly silylated with octyltrichlorosilane did not provide pillared carbons; therefore, we first silylated graphite oxide with octyltrichlorosilane molecules and then with 3-aminopropytriethoxysilane molecules possessing smaller 3-aminopropyl groups, which are removed during heating.

2. Experimental

Graphite oxide (abbreviated as GO) was prepared from graphite powder by the method based on the Brodie’s one [20] according to our previous studies [21,22]. This procedure was repeated 5 times and GO with the composition of C₄O₆₆H₃₂ was obtained. The obtained GO was silylated with octyltrichlorosilane (C₈SiCl₃) and then 3-aminopropytriethoxysilane (APS) by the following two-step methods.

GO (100 mg) was mixed with n-butylamine (C₄H₉NH₂, hereafter abbreviated as C₄, 0.5 ml; 32 molecules per GO unit) as an exfoliating reagent in a sealed glass vial under dry argon and the resulting dispersion was sonicated, then heated at 60 °C for 1 h.
Dry toluene (5 ml, water content < 30 ppm) was added to this dispersion under an argon atmosphere and the solution was again sonicated. The silylating reagent of C8SiCl3 (13 molecules per C8 unit of GO) were added to the toluene solution containing GO and C4 and then allowed to stand for 1 day at 60 °C. After centrifugation, the precipitate was washed with dry toluene, ethanol and then acetone. The resulting sample is abbreviated as (C8Si)xGO where the letter “x” means the content of bound silane per C8 unit of GO. Assuming that it contains 0.4 n-butylamine per C8 unit of GO, the “x” value is determined to be 0.41, based on the weight of the residual SiO2 after thermogravimetric analysis.

The (C8Si)0.41GO sample was then silylated with APS in a similar manner reported in our previous studies [10,11,23]. Typically, silylated GO samples (50 mg) were put in toluene (7.5 ml) and various amounts of silylating reagents (0.01–3.3 ml; APS/C8 unit of GO of 0.22–72) were added. The mixture was kept at 60–110 °C for 1–2 day. After reaction, the products were washed with toluene and acetone several times and then dried at 60 °C under vacuum for 5 h. The temperature increasing rate was 1 °C/min. These samples were analyzed by X-ray diffraction (Rigaku, Rint-2100, CuKα), FT-IR (Nicolet Avatar 360, KBr method), thermogravimetric (TG; Shimadzu, TGA-50), scanning electron micrograph (SEM; JEOL, JSM-5600) and nitrogen adsorption (Bel Japan Inc., BELSORP-miniII, at 77 K) measurements. TG measurement was performed under air with the temperature increase rate of 5 °C/min between room temperature and 800 °C.

3. Results and discussion

3.1. Silylation of GO with octyltrichlorosilane and then 3-aminopropyltriethoxysilane

Fig. 1 shows the X-ray diffraction patterns of (C8Si)x0.41GO silylated with various amounts of APS. The diffraction peak observed for the pristine (C8Si)x0.41GO at 2θ = 6.0° (d = 1.47 nm) shifted to lower angles as the increase of the amount of the added APS and reached the lowest value of 2θ = 3.36° (d = 2.63 nm), when APS/C8 unit of GO reached 4.6. Then, the diffraction peak shifted to higher angle as the increase in the amount of the added APS.

Fig. 2 shows the IR spectra of GO, (C8Si)x0.41GO and (C8Si)x0.41GO silylated with APS/C8 unit of GO = 4.6 (sample (d) in Fig. 1). The absorption peak at 900 cm⁻¹ due to Si–OH groups almost disappeared after reaction with APS. This indicates that the APS molecules are attached to silylated GO via Si–O–Si bonding. The APS molecules can also intercalate into (C8Si)x0.41GO both by hydrophobic interaction and hydrogen bonding between hydroxyl and amino groups. When the amount of the added APS was high, the APS molecules hydrogen-bonded to Si–OH groups could prevent the access of ethoxy groups in the other APS molecules and result in the decrease in the reaction rate. In addition, it has been reported that the amines can remove oxygen from GO especially at elevated temperatures [23]. The reduced number of oxygen functional groups on GO layers leads to the decrease in the reaction sites for APS molecules; accordingly the interlayer spacing of C8SiGO prepared with higher APS/C8 unit of GO ratios became smaller.

Fig. 3 shows the thermogravimetric analysis data of GO, C8SiGO and (C8Si)x0.41GO silylated with APS/C8 unit of GO = 4.6. The steep decrease in the weight of GO at 250 °C indicated that most of the oxygen functional groups in GO were removed at this temperature. In case of (C8Si)x0.41GO, this weight decrease was commonly observed and the gradual weight decrease between 300 and 500 °C due to the removal of alkyl chains was also observed. On the other hand, an additional weight decrease around 190 °C was observed for APS-(C8Si)x0.41GO, which is ascribed to the conversion of ethoxy groups in APS to hydroxyl groups [23]. The weight decrease due to the removal of oxygen containing groups shifted to a higher temperature and it cannot be distinguished from that of the decomposition of organic groups including alkyl chains and 3-aminopropyl groups. This suggests that the release of gases during the removal of oxygen functional
groups from GO layers was in more controlled manner and the exfoliation of GO layers was suppressed. The other feature was the higher water content estimated from the weight decrease below 100 °C (5.3%) than that of (C₈Si)₀.₄₁GO. The introduction of more hydrophilic amino groups in GO is responsible for this higher water content. The silicon content calculated from the weight of residual silica after TG measurement reached a value of 14.1%. The amount of the residual ethoxy groups was estimated from the weight of residual silica after the APS/C₈ unit of the prepared carbon became smaller and almost disappeared for the sample prepared from (C₈Si)₀.₄₁GO-APS with larger interlayer spacings, the diffraction peak due to the residual carbon was dominantly observed, as shown in Fig. 4 (a)–(c), (f) and (g). On the other hand, samples prepared from (C₈Si)₀.₄₁GO-APS with larger interlayer spacings, the diffraction peak due to the residual carbon became smaller and almost disappeared for the sample prepared from (C₈Si)₀.₄₁GO-APS reacted with the APS/C₈ unit of GO ratio of 4.6. For this sample, the diffraction peaks at 2θ = 11.26 (d = 0.786 nm) and 16.86° (d = 0.526 nm) were observed, which can be ascribed to (002) and (003) diffraction lines of pillared carbon. The morphology of the resulting sample observed by scanning electron micrograph (SEM) was almost identical to that of the pristine GO and no deposits derived from the condensation of APS molecules were observed, as was the case for pillared carbons prepared from GO repeatedly silylated with methyltrichlorosilane [19]. The interlayer spacing of the present pillared carbon was 1.58 nm, which was larger than those obtained previously (1.25–1.37 nm) [10–12,19]. Considering that previous pillared carbons were mostly prepared from GO silylated with only one kind of silylating reagent, suggesting that the different sizes of the organic groups attached to GO layers are important for the increased interlayer spacing.

3.3. Adsorption properties of pillared carbons

Fig. 5 shows the nitrogen adsorption isotherm of the pillared carbon with an interlayer spacing of 1.58 nm (sample (d) in Fig. 5). The adsorbed amount of N₂ steeply increased at the low relative pressure and reached an almost constant value at higher relative pressures. The isotherm is classified to type I, indicating that this sample contains mainly micro pores. The BET surface area reached a relatively high value of 756 m²/g. This was in contrast with the results obtained for the pillared carbons prepared from GO silylated with 3-aminopropyldiethoxymethylsilane, which possessed both micro- and mesopores, and the BET surface area was only 240 m²/g [10–12]. Since the content of silylating reagents in GO was similar to those reported previously, the larger interlayer spacing of the present pillared carbon indicates the lower density of pillars in the gallery between carbon layers. This is responsible for the formation of the pillared carbon with a higher BET surface area. Moreover, the pillars are uniformly distributed on the carbon layers and the two dimensional space between them are well divided.

Fig. 6 shows the α₃ comparison plot using the data of carbon black as a reference [24,25]. An upward swing (filling swing) indicating that this sample possessed ultramicropores with pore width below 0.7 nm was observed at low α₃ values. Based on the slope of the straight line from the origin shown in Fig. 6, the total surface area was calculated to be 740 m²/g. Based on the slope and the intercept of the dotted line, micropore volume and external surface area were calculated to be 0.27 ml/g and 16 m²/g, respectively. The pore width...
was estimated to be 0.74 nm, assuming the slit type pores. This value was slightly larger than that expected from the upward swing, which indicates the pore size of smaller than 0.7 nm. When the surface of the pillars is also available for the adsorption of nitrogen molecules in addition to that of the carbon layers, the slit type pore is no longer applicable for that of pillared carbons and the pore width should be smaller.

4. Conclusions

Microporous pillared carbon with an interlayer spacing of 1.58 nm was obtained from the pyrolysis of GO silylated with octyltrichlorosilane and then with 3-aminopropyltriethoxysilane. Appropriate amounts of the silylating reagents should be attached to the layers of GO to obtain pillared carbons, otherwise silica/carbon composites were formed. The adsorption isotherm of pillared carbon was type I, indicating that it was microporous. The different molecular lengths of 3-aminopropyl and octyl groups in silylated GO seemed to play an important role to obtain pillared carbon with a large interlayer spacing and create micropores. The BET surface area reached a relatively large value of 756 m²/g and the calculated pore width was 0.74 nm.

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