

PREPARATION AND PROPERTIES OF MICROPOROUS PILLARED CARBONS

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Introduction

Carbons with controlled pores and high surface area are attracting much attention for the support of catalysts, adsorbents, electrode of electric double layer capacitor, etc. In this context, we have successfully prepared pillared carbons by pyrolysis of silylated graphite oxide in which the adjacent carbon layers are connected by silica or silsesquioxane pillars containing methyl groups *via* C-O-Si bonding. However, the BET surface area of them was unexpectedly very small, less than 240 m²/g [1]. Our previous results suggested that this was due to the narrow space between pillars for nitrogen molecules to pass. In order to increase the surface area and to create more pores in pillared carbons, it would be necessary to reduce the width of pillars, for example, by replacing methyl groups in the pillars with smaller functional groups such as hydroxyl groups or introducing defects into them. In this study, pillared carbons with higher surface area were prepared by the pyrolysis of graphite oxides silylated by two different silylating reagents without methyl groups.

Experimental

Graphite oxide (abbreviated as GO) was prepared from graphite powder (Aldrich, or natural) by the method based on the Brodie's one according to our previous studies [2,3] and GO with compositions of C₈O_{4.6} H_{3.0} were obtained. The obtained GO was silylated with octyltrichlorosilane (C₈SiCl₃) and then 3-aminopropyltrimethoxysilane (APS) by the following two-step methods.

GO was mixed with n-butylamine (C₄H₉NH₂, hereafter abbreviated as C₄) in a sealed glass vial under dry argon and the resulting solution was sonicated, then heated at 60°C for 1 h. Dry toluene was added to this solution under an argon atmosphere and the solution was again sonicated. The silylating reagent of C₈SiCl₃ was added to the toluene solution containing GO and n-butylamine 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 samples are abbreviated as (C₈Si)_xGO where the letter "x" means the content of bound silane per C₈ unit of GO. The x values were determined based on the weight of residual SiO₂ after thermogravimetric analysis, assuming that they contain 0.4 n-butylamine per C₈ unit of GO.

These (C₈Si)_xGO samples were then silylated by APS in a similar manner reported in our previous study [1]. Typically, silylated GO samples (50 mg) were put in toluene and various amounts of silylating reagents were added. The mixture was kept at 60 - 110°C for 1 - 2 days. After reaction, the products

were washed with toluene and acetone several times and then dried at 60°C under vacuum overnight. Pyrolysis of silylated GO was performed by heating it at various temperatures between 500°C under vacuum for 5h. The temperature increasing rate was 1 °C/min. These samples were analyzed by X-ray diffraction, FT-IR, thermogravimetric, and nitrogen adsorption measurements.

Results and Discussion

Silylation of GO

Fig.1 shows the X-ray diffraction patterns of (C₈Si)_{0.59}GO silylated with APS at various temperatures for 1 or 2 days. The diffraction peak shifted to lower angle as the increase in the reaction temperature or the reaction time and reached 2θ=2.48° (d=3.56 nm) at 100°C. Then, it shifted to a lower angle of 2θ=3.54° (d=2.50 nm) at 110°C, which was very similar to that obtained from (C₈Si)_{0.41}GO. The silicon content in APS-(C₈Si)_{0.59}GO increased with the increase in the interlayer spacing and reached 14.7 %.

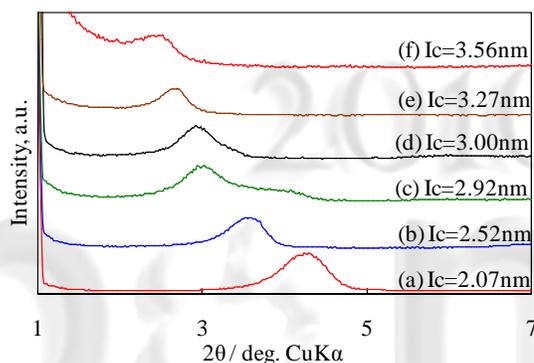


Fig.1 X-ray diffraction patterns of C₈SiGO-APS prepared at 60°C for (a): 1 and (b): 2 days, and at (c): 70, (d): 80, (e): 90 and 100°C for 1 day

Preparation of pillared carbons

Fig.2 shows the X-ray diffraction patterns of APS-(C₈Si)_{0.59}GO with different interlayer spacings after heated at 500°C under vacuum. A broad diffraction peak around 2θ=11° due to the pillared carbon was observed for the sample (A) obtained from APS-(C₈Si)_{0.59}GO with a smaller interlayer spacing, however, that around 2θ=24° derived of residual carbon was also observed. The diffraction peak around 2θ=11° became sharper and that around 2θ=24° almost disappeared for the samples from APS-(C₈Si)_{0.59}GO with a larger interlayer of nm. The diffraction peak due to pillared carbon slightly shifted to lower angle as the increase in the interlayer spacing of the APS-(C₈Si)_{0.59}GO samples. Then, it again became broader and almost disappeared for the sample obtained from APS-(C₈Si)_{0.59}GO with the interlayer spacing of 3.56 nm. As shown in our previous paper, in order to obtain pillared carbon without residual carbon, sufficient amounts of silylating reagents should be attached to the layers of GO. The above result indicates that too much silylating reagents attached to the layers of GO also prevent the formation of pillared carbons.

When the silylated GO contains too much silylating reagents in them, the distance between the adjacent silylating reagents decreases. In such a case, the size of the pillar formed as the result of heating is expected to increase. When the pillars become larger, it would be more stable to form randomly polymerized materials which can not be well accommodated in the gallery between the carbon layers, leading to the formation of composite of residual carbon and silica rather than pillared carbons.

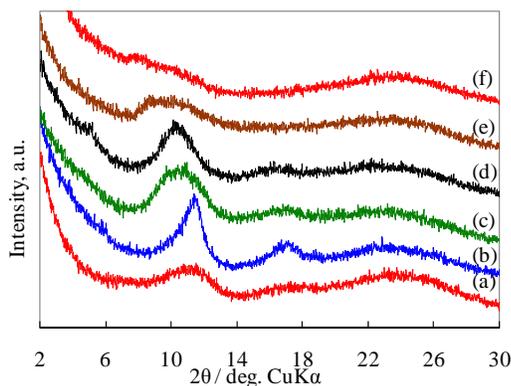


Fig.2 X-ray diffraction patterns of $C_8SiGO-APS$ heated at $500^\circ C$.

Adsorption properties of pillared carbons

Fig. shows the nitrogen adsorption isotherm of pillared carbon obtained from $APS-(C_8Si)_{0.41}GO$ with an interlayer spacing of 2.63 nm. The adsorbed amount of N_2 steeply increased at the low relative pressure and reached an almost constant value. The isotherm is classified to type I, indicating that this sample contains microporosities. The BET surface area reached a relatively high value of $756\text{ m}^2/\text{g}$. This was in contrast with the results obtained for the pillared carbons prepared from GO silylated with 3-aminopropyldiethoxymethylsilane which possessed both micro and mesoporosities, and the low BET surface area were less than $240\text{ m}^2/\text{g}$ [1].

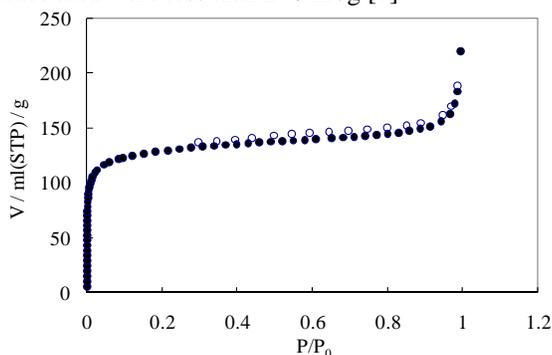


Fig.3 Adsorption isotherm of pillared carbon with an interlayer spacing of 1.56 nm.

Fig.4 shows the α_s -comparison plot of pillared carbon prepared from the $APS-(C_8Si)_{0.41}GO$ with an interlayer spacing of 2.63 nm, using the data of carbon black and silica as references [4]. The amount of adsorbed N_2 molecules

started to increase when α_s value reached 0.25 when the datum of the carbon black was used as a reference. On the other hand, it started to increase steeply at very low α_s values, when the datum of the silica was used as a reference. Then the two curves became almost identical when the α_s values were larger than 0.5. This suggests that the surface of pillared carbon consisting of both carbon and silicon containing species is between carbon black and silica.

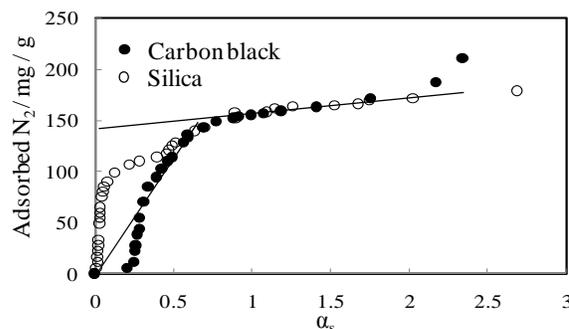


Fig.4 α_s plot of the pillared carbon with an interlayer spacing of 1.56 nm.

Fig.5 shows the BET surface area of pillared carbons as a function of the interlayer spacing of them, together with those obtained in our previous studies. It increased with the increase in the interlayer spacing and reached a maximum value of $756\text{ m}^2/\text{g}$ for the sample with an interlayer spacing of 1.65 nm. Then it slightly decreased, probably because too much pillars existing between the carbon layers prevented the access of N_2 molecules to the pores.

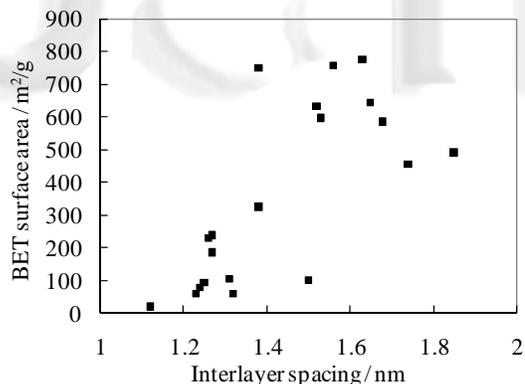


Fig.5 Relationship between interlayer spacing and BET surface area of pillared carbons.

References

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