

PREPARATION OF POROUS CARBON BY PYROLYSIS OF SILYLATED GRAPHITE OXIDE

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Abstract

Starting from the graphite oxide silylated by 3-aminopropylmethyldiethoxysilane, porous carbons containing silica with layered structure were obtained. They possessed both microporosities and mesoporosities existing most likely between the carbon layers and the BET surface area reached 226 m²/g. These types of carbons were obtained only when the silicon content in the initial silylated graphite oxide was larger than 12%.

Introduction

Carbon materials with a large surface area and controlled pore sizes are very useful for adsorbents, support of catalysts, electrode material of electric double layer capacitors, etc. Activated carbons are well known for this type of carbons, however, it is rather difficult to control the pore size and structure of them. Therefore, recently, the synthesis of various carbons with controlled pore structure and high surface area such as templated carbons has been reported [Lee 1999, Ma 2000, Ryoo 1999]. Pillaring is one of the technique to open the pore structure of various layered materials such as clays, etc. In this context, several attempts to obtain pillared carbons starting from the intercalation compounds of graphite oxide (GO) have been reported recently [Wang 2002, Morishige 2005]. In these reports, carbon/silica or carbon/iron oxide composites with high surface area was obtained. However, the order of carbon layers was almost lost in them probably because the decomposition of the intercalation compounds occurred prior to the transformation of GO to carbons. The intercalated species was then aggregated and mixture of oxide and carbon was formed. On the other hand, we have recently reported silylation of GO using various silylating reagents [Matsuo]. In the obtained silylated GOs, the intercalated species are tightly bonded to the layer of GO by covalent bonding and, accordingly, it is expected that the aggregation of intercalated species is prevented at low temperatures. Therefore, thermal decomposition of these materials would give a novel carbon with a layered structure, so called "pillared carbon". This type of material would possess pores between the carbon layers as was reported for various layered oxides. In this study, silylated GO was thermally decomposed and the resulting material was investigated.

Experimental

GO was prepared by oxidizing graphite powder (Aldrich, 1-2 μm) with KClO₃ in fuming nitric acid at 60°C, based on the Brodie's method and GO with the composition of C₈O_{4.5}H_{3.0} was obtained. GO (100 mg) was silylated by 3-aminopropylmethyldiethoxysilane (NH₂C₃H₆SiCH₃(OC₂H₅)₂, hereafter abbreviated as AP2ES; 0.87 ml) in toluene (20 ml) under reflux for 1 - 20 days [Matsuo 2007]. After centrifugation, the precipitate was washed with acetone several times. The obtained samples (abbreviated as GO-AP2ES(n), n:reaction time / days) were dried at 60°C under reduced pressure for 12 h. The Si content calculated from the weight of residual SiO₂ after thermogravimetric measurement and, 10 - 15.0 % were obtained. Pyrolysis of silylated GO was performed by heating it at 500 °C under vacuum for 5h. The products (abbreviated as PGO-AP2ES(n)-T; T: temperature) were treated by 47% HF aqueous solution overnight, in order to remove Si containing species. These samples were analyzed by X-ray diffraction (Rigaku, Rint-2100, CuKα), FT-IR (Nicolet Avatar 360 KBr method), and nitrogen adsorption (Bel Japan Inc., BELSORP-mini II, 77K) measurements

Results and discussion

Figure 1 shows the X-ray diffraction patterns of GO-AP2ES(6) and PGO-AP2ES(6) pyrolyzed at various temperatures. The diffraction peaks at 6.90 and 13.56° were observed for GO-AP2ES(6), which were indexed as (001) and (002) lines, and the interlayer spacing was calculated to be 1.29 nm [Matsuo 2007]. The diffraction peaks became very broad at 400°C and then relatively sharp peaks at 2θ=14.38 and 21.98° which can be indexed as (002) and (003) lines appeared after pyrolysis at 450°C. These peaks slightly shifted to lower angles as the temperature increased and then disappeared at 600°C, providing a new peak at 2θ=25.3°. This peak is ascribed to the carbon formed as the result of de-intercalation of silicon containing species. The absorption peaks at 2920 cm⁻¹ due to -(CH₂)-groups observed in the IR spectrum of pristine GO-AP2ES(6) disappeared above 450°C, which indicates that 3-aminopropyl or ethoxy groups were eliminated from the sample. The X-ray diffraction peaks

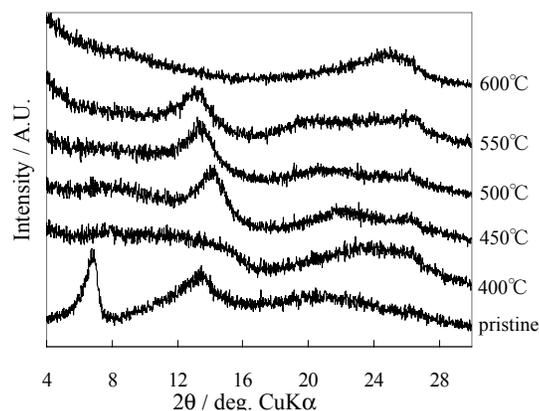


Figure 3. X-ray diffraction patterns of GO-AP2ES before and after pyrolyzed at various temperatures.

observed for PGO-AP2ES(6)-500 disappeared after HF treatment and a new peak at 26.1° ($d=0.34$ nm) was observed, as shown in Figure 2. The silicon-containing species easily dissolves in HF solution, therefore, this peak is ascribed to the residual carbon. These suggest that the PGO-AP2ES samples obtained between 450 and 550°C possess layered structures and include silicon-containing species between the carbon layers. The interlayer spacing was calculated to be 1.22 – 1.33 nm and the size of silicon-containing species was about 0.88 - 0.99 nm. The silicon contents determined from the TG data were 19.0 % and the Si/C ratios were 6.2, based on the elemental analysis of carbon and silicon contents for PGO-AP2ES(6)-500. These types of carbon were obtained only when GO-AP2ES with a silicon content higher than 12.0 % was pyrolyzed, otherwise a diffraction peak at $2\theta=25^\circ$ due to carbon appeared clearly at the same time. An appropriate amount of silicon was needed in order to maintain regularly stacked layered structure.

Figure 3 shows the nitrogen adsorption isotherm of PGO-AP2ES(6)-500, together with those for GO-AP2ES(6) and PGO-AP2ES(6)-500 after HF treatment. The isotherm of PGO-AP2ES(6)-500 after HF treatment presents type II and the amount of adsorbed N_2 was very low. The BET surface areas were only 21 and m^2/g . On the other hand, the isotherm of PGO-AP2ES(6)-500 presents the shape of type IV. The evident adsorption hysteresis suggests the existence of mesoporosity. A steep increase at $P/P_0 < 0.1$ was observed, indicating the existence of micropores. The total specific surface area determined by the Brunauer-Emmett-Teller (BET) method was 226 m^2/g . These strongly suggest that the outer surface of carbon is not responsible for the mesoporosity and microporosity, and they exist most likely between the carbon layers of PGO-AP2ES samples. The desorption branch does not close with adsorption branch, indicating that there are very narrow micropores in which the diffusion of nitrogen molecules needs activation energy. The shape of the isotherms for PGO-AP2ES-500 samples with different silicon contents were very similar to that of PGO-AP2ES(6)-500.

In conclusion, starting from silylated GOs, porous carbons containing silica with layered structure were obtained. They possessed microporosities and mesoporosities existing most likely between carbon layers.

Acknowledgment

The authors are grateful to Prof. T. Yazawa of University of Hyogo for his assistance in nitrogen adsorption measurements.

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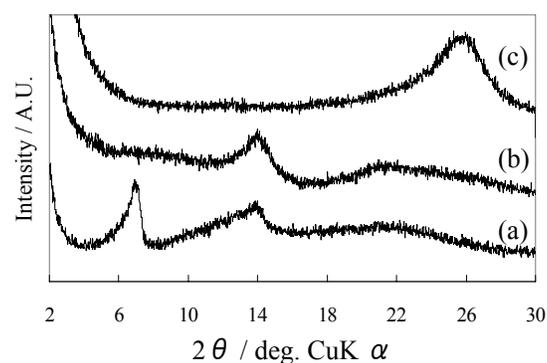


Figure 2. X-ray diffraction patterns of (a): GO-AP2ES(6), (b): PGO-AP2ES(6)-500 and (c): PGO-AP2ES(6)-500 after immersion in HF.

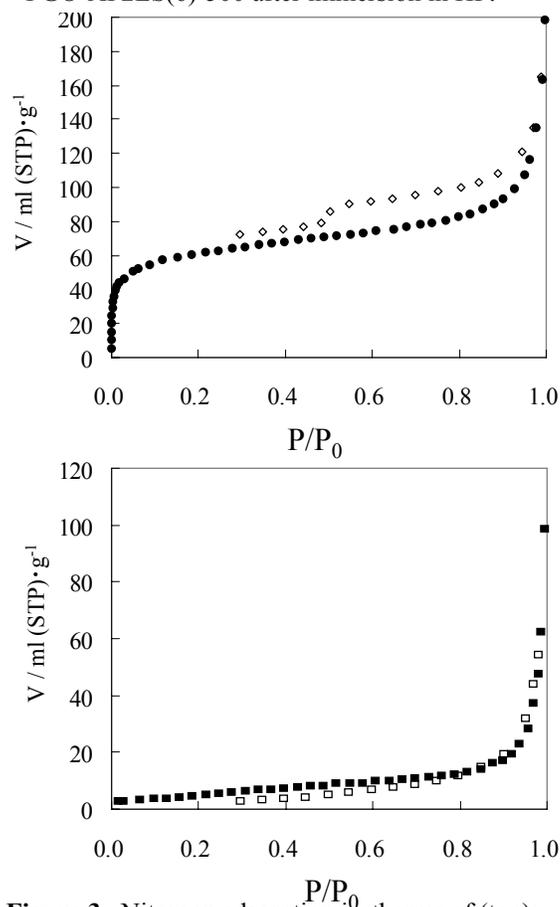


Figure 3. Nitrogen adsorption isotherms of (top): PGO-AP2ES(6)-500 and (bottom): PGO-AP2ES(6)-500 after HF immersion. The filled and open marks indicate the adsorption and desorption branches, respectively.