

The Preparation of Flaky Layered Carbon by Using Layered Silicate Template

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In recent years, the preparation and application of nanostructure carbon materials such as carbon nanotube and nanoporous carbon has attracted increasing interests.¹⁻⁶ We now report on the preparation of flaky layered carbon by using layered silicates as template. These layered carbons should be applicable potentially in technical field such as the electronics, catalytic and hydrogen-storage system. Layered silicates have exchangeable cations such as Na⁺, K⁺, Ca²⁺ and Mg²⁺ in the interlayer space. These cations have a role as good electron acceptor for electron donors. Their acid treatment also produce silanol groups by the ion exchange of cations for H⁺ and this silanol groups can have a role as hydrogen-bonding sites for various organics. Polyaromatics, which are good electron donor for the interlayer cations or silanol group, can easily intercalate into the gallery interacting with interlayer cations or silanol groups. Since polyaromatics in the gallery of nm scale may arrange regularly with sandwich structure, the pyrolysis in the inert condition can produce well-developed flaky layered carbon in the gallery.

In this study, kenyaite was used as layered silicate template. Kenyaite is composed of very soluble pure SiO₂ in HF and strong alkali solution and can be synthesized easily in hydrothermal condition. Residual oil (pyrolyzed fuel oil: abbreviated as PFO) from LG Petroleum Chem. Co. (Korea) was also used as polyaromatic carbon source. PFO was obtained from pyrolysis of naphtha and viscous liquid composed of long chain hydrocarbon and various polyaromatics. Here, synthetic Na-kenyaite was prepared by the reaction of NaOH/Na₂CO₃-SiO₂ system under hydrothermal condition using method analogous to those described by Kwon *et al.*⁷ H-kenyaite was also prepared by the ion exchange of Na-kenyaite for H⁺ in 0.1 N HCl solutions using previously reported method.⁸ Na-kenyaite and H-kenyaite were mixed directly with PFO (1 : 1 as weight ratio) for 1 h, respectively. Each mixtures were pyrolyzed in crucible with cover for 1 h at 600 °C. Resultant black cakes are composed of layered carbon-layered silicate nanocomposite (abbreviated as LC-LSN) piling carbon film in layers of kenyaite. Silicate frame was dissolved from the LC-LSN by dispersing for 1 h in HF (15%) solution. Here, strong alkali solution such as NaOH, KOH and Na₃PO₄ can also use for dissolution of

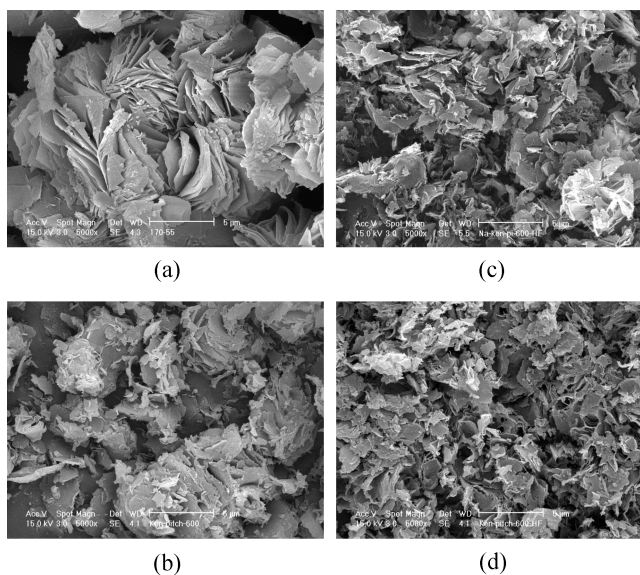


Figure 1. SEM morphologies for the Na-kenyaite, LC-LSN and FLC: (a) Na-kenyaite, (b) LC-LSN prepared from Na-kenyaite template, (c) FLC prepared from Na-kenyaite template, and (d) FLC prepared from H-kenyaite template.

silicate framework. The slurry was filtered, washed with deionized water and air-dried. The dried black powder allows porous flaky layered carbon (abbreviated as FLC) with open gallery between carbon sheets of layered structure.

Figure 1 shows SEM morphology of LC-LSN and FLC prepared by using Na-kenyaite and H-kenyaite template. LC-LSN exhibits particle morphology characteristic of Na-kenyaite or H-kenyaite, which is more or less spherical nodules of plate-like crystals or open aggregates of well-developed platelets. SEM morphology for FLC show clearly that the removal of silicate frame from LC-LSN brought about no change from the morphology of original LC-LSN. This implies that kenyaite have a perfect role as template. FLC particles are separated with uniform size of 2-3 μm and composed of well-developed flakes. This particle morphology is very unique among carbon materials. EDS analysis confirmed that FLC consisted of pure carbon.

Figure 2 shows XRD powder diffraction patterns of LC-LSN and FLC prepared by using Na-kenyaite and H-kenyaite template comparing with carbon black, activated carbon and synthetic graphite. Basal spacing of LC-LSN obtained from Na- and H-kenyaite was 2.0 nm and 1.80 nm,

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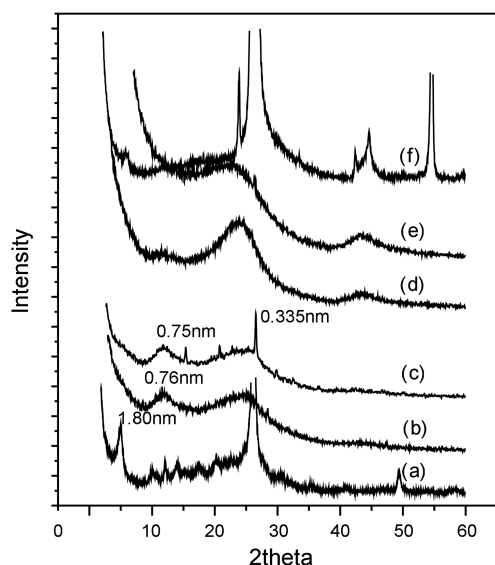


Figure 2. XRD powder diffraction patterns for the LC-LSN and FLC comparing with commercial carbon materials: (a) LC-LSN prepared from Na-kenyaite template, (b) FLC prepared from H-kenyaite template, (c) FLC prepared from Na-kenyaite template, (d) carbon black, (e) activated carbon, and (f) synthetic graphite.

respectively. Since basal spacing of template was also decreased to 1.80 nm (Na-kenyaite) and 1.65 nm (H-kenyaite) by the heat treatment for 1 h at 600 °C, gallery height of Na-kenyaite and H-kenyaite was increased to 0.20 nm and 0.15 nm, respectively by piling carbon films between layers. This implies that carbon in the gallery arrange with monolayer thin film of ~0.2 nm thickness. The removal of layered silicate template from LC-LSN resulted in the appearance of new broad peak at 11.7 degree (basal spacing is 0.76 nm), which is quite different from carbon black and activated carbon. New broad peak in FLC is attributed to disordered open gallery formed by the removal of template. In particular, the peak characteristic of graphite appears newly in the sample prepared by Na-kenyaite. It is very exceptional result that the graphite crystal can be produced by the heat treatment for 1 h at 600 °C, because synthetic graphite can be prepared by the heat treatment for a long time at 2500-3000 °C. This implies that Na⁺ ion in the gallery may promote the transformation of graphite crystal from PFO,

because Na⁺, in this two-dimensional space of nano scale, can arrange PFO in regular planar structure that is easy to transform into graphite. BET surface area of LC-LSN was only 50-80 m²/g, whereas FLC materials exhibited large increase of 160 m²/g (Na-kenyaite) and 240 m²/g (H-kenyaite) depending upon a sort of template. H-kenyaite template results in large increase in surface area than Na-type. Here, large surface areas are attributed to the gallery that is formed by removing silicate templates. These flaky layered carbons with high surface area may be highly applicable to conductive and secondary battery electrode material. Further studies should be conducted on the synthetic condition, physical properties and application of FLC.

In conclusion, porous layered carbons with well-developed flake structure were successfully prepared by using layered silicate template. The gallery of layered silicate is composed of two-dimensional spaces with nano scale, which can have a role as nano reactor for chemicals introduced into the gallery. It confirmed that PFO, in this nano reactor, could be transformed easily to layered carbon or graphite structure by the heat treatment, allowing layered carbon-layered silicate nanocomposite (LC-LSN) piled carbon film or graphite sheet in layers of layered silicate. The removal of template from LC-LSN resulted in separated and well-developed flaky layered carbon or graphite with large surface area of 160-240 m²/g, which was quite different from carbon black and activated carbon.

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