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Novel synthesis of polymer and carbonaceous nanomaterials *via* a micelle/silicate nanostructured precursor†

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Mesoporous carbonaceous materials with relatively high surface area have been synthesized by a new method composed of *in situ* polymerization of divinylbenzene in the hydrophobic phase of a hexagonally arrayed micelle/silicate nanocomposite and subsequent carbonization and hydrofluoric acid treatments, while rod-like carbons were obtained from a direct incorporation of divinylbenzene into the mesopores of MCM-41.

Recently, there has been intensive interest in the fabrication of nano- and meso-structured materials consisting of organic and inorganic frameworks. In particular, the use of surfactant templates to control the structure of inorganic solids has proven successful for tailor-making mesoporous materials such as mesoporous silica (MPS).[1,2] In the case of the synthesis of MCM-41 as representative of MPSs, a cylindrical micelle serves as a template for assembly and subsequent condensation of silicate ions to give a hexagonally arrayed surfactant/silicate composite mesophase that can be converted into MPS by a heat-treatment.[3] In the present study, the hydrophobic phase in a micelle/silicate nanocomposite precursor was used as a reaction field for the regulated polymerization of an organic monomer. When the polymerization reaction is carried out in aqueous micelle solution, spherical latex polymer particles are usually obtained exclusively. There is a limitation to control the morphological mesostructure of polymers by using aqueous micelle solutions because of the dynamic structure change of micelle in aqueous phase. On the other hand, the micelle phase in the micelle/silicate composite has a potential for nanoscale polymerization since the micelle structure is fixed and stabilized by the surrounding silicate layer. Here we describe a novel synthetic strategy for the preparation of nanostructured polymer precursors and carbonaceous materials, which is composed of the incorporation of polymerizable monomer (divinylbenzene, DVB) into the hydrophobic phase in a micelle/silicate composite, *in situ* polymerization and carbonization processes. Mesoporous carbonaceous materials with high surface area were finally obtained *via* the micelle/DVB-polymer/silicate nanocomposite precursor.

3 mmol of cetylpyridinium chloride ($C_{16}PyCl$) was added into 50 mL of water as surfactant and then the solution was stirred with optional heating to obtain a clear micelle solution. 4 mL of divinylbenzene (DVB), which was purified by washing three times with 10% aqueous NaOH, 10% aqueous $NaHSO_4$ and water, was mixed with 20 mg of 2,2′-azobis(isobutyronitrile) (AIBN) and then the DVB solution was added dropwise to the $C_{16}PyCl$ solution under stirring at room temperature. After the DVB-containing micelle solution became clear, an aqueous sodium silicate (2.5 mmol) solution was added dropwise under stirring and then the pH of the solution was adjusted to around 1.0 by adding 5 mL of aqueous HCl. The molar composition of final mixture was $SiO_2:C_{16}PyCl:HCl:DVB:AIBN:H_2O = 1:0.12:2:1.0:0.012:180$. After further stirring for 3 h at room temperature, precipitated product was filtered off and washed with water thoroughly. The as-synthesized micelle/DVB/silicate composite was subjected to heating at 70 °C for 6 h and at 110 °C for 1 day in an oven to polymerize the incorporated DVB monomer. The complete polymerization of DVB in the composite was confirmed by IR measurements (Perkin-Elmer 1650 FTIR spectrometer) that showed the disappearance of the IR peak of the vinyl group at 1628 cm^{-1} after the heat-treatment at 110 °C for 1 day. The obtained products were characterized by means of X-ray diffraction measurement (XRD, Rigaku LINT-2200, Cu-Kα) and thermogravimetry (TG, Shimadzu DTG-50). The micelle/silicate composite without DVB, which could be converted into MCM-41 type mesoporous silica by air-calcination at 550 °C for 6 h,[4] showed distinct XRD peaks assignable to (100), (110) and (200) planes of the hexagonally arrayed mesostructure after heat-treatment at 70 °C for 6 h (Fig. 1(a)). The DVB-containing micelle/silicate composite obtained after heating at 70 °C clearly showed XRD peaks of the (100), (110) and (200) planes due to a hexagonal arrayed mesostructure (Fig. 1(b)). The value of the basal plane spacing (*d*) of the micelle/DVB/silicate composite was 48 Å, which was larger than that of the micelle/silicate composite without DVB (*d* = 34 Å). After the heat-treatment at 110 °C for 1 day, the XRD pattern was almost preserved although the peak intensity and *d* value (46 Å) were

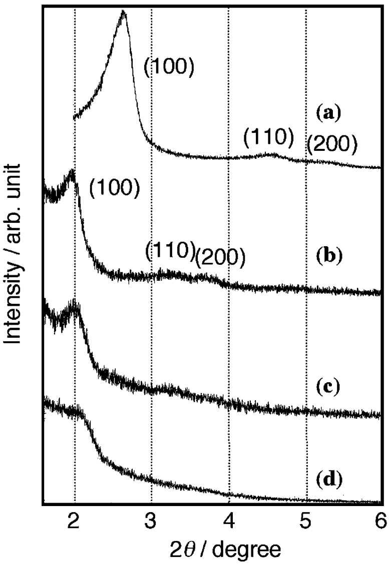

Fig. 1 XRD patterns of (a) micelle/silicate composite after heating at 70 °C for 6 h in air and (b)–(d) micelle/DVB/silicate composites; (b) after heating at 70 °C for 6 h in air, (c) after heating at 110 °C for 1 day in air, (d) after heating at 600 °C for 0.5 h in N_2 gas flow.

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† Electronic supplementary information (ESI) available: IR spectra and adsorption–desorption isotherms. See http://www.rsc.org/suppdata/cc/b2/b204622a/

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reduced slightly (Fig. 1(c)). These results indicate that the micelle/DVB/silicate composite has a hexagonally arrayed mesostructure similar to the micelle/silicate precursor of MCM-41 and the incorporation of DVB monomer into the micelle/silicate nanocomposite resulted in the expansion of the periodic micelle/silicate composite mesostructure as reported in the synthesis of mesoporous silica with large mesopores using the auxiliary mesitylene.[5,6] The incorporated DVB monomer polymerized in the hydrophobic phase of the micelle in the composite with heating up to 110 °C while the expanded hexagonal mesostructure was retained. In the TG measurements, the sample after heating at 110 °C showed two-step weight losses with heating in air up to 800 °C: the first weight loss at the temperature range 250–300 °C (32 wt%) corresponds mainly to the thermal decomposition of surfactant[5] and the second weight loss at 350–600 °C (37 wt%) to decomposition of DVB polymer (Fig.2(a)). The amount of DVB molecules surviving in the micelle phase after the 110 °C heating was estimated to be *ca.* 3.0 molecules per C_{16}Py surfactant molecule from the DG weight ratio (37 : 32) and the ratio of molecular weight (DVB/C_{16}py = 0.33). The difference of *d* value (1.4 nm) between the DVB/micelle/silicate (Fig. 1(b)) and micelle/silicate (Fig. 1(a)) would be plausible since the sum length of three DVB molecules is in the range of 1–3 nm though it depends on the molecular arrangement, orientation and polymerization degree.[7]

When the TG measurements of the micelle/DVB-polymer/silicate composite was performed under N_2 gas flow, two-step TG weight losses similar to those in air were observed, but the second weight loss (25%) was less than in air (Fig. 2(b)). The difference of weight loss between in air and in N_2 gas corresponds to the weight of residue as a carbonaceous material. The bulk DVB polymer which was obtained by polymerization from only DVB/AIBN solution showed a weight loss due to the thermal decomposition and carbonization of DVB polymer around 400 °C with *ca.* 30% yield of carbonaceous material at 600 °C. The carbonization yield of DVB polymer in the micelle/silica composite system was also 32% at 600 °C, suggesting that the incorporated DVB polymer in the composite was successfully converted into carbonaceous materials under heating in N_2 to yield a carbon/silica composite. The carbon/silica composite obtained at 600 °C showed a broad XRD peak around $2\theta = 2°$ (Fig. 1(d)), the *d* value of which was smaller than that of micelle/DVB-polymer/silicate composite after heating at 110 °C but larger than that of mesoporous silica synthesized from the micelle/silicate composite without DVB. This indicates that the micelle/DVB-polymer/silicate composite was irregularly merged to some extent during the carbonization process to yield a disordered carbon/silica composite nanostructure.

The carbon/silica nanocomposite obtained by heating at 600 °C for 0.5 h was treated with an aqueous HF solution to dissolve the silica part. The residual carbonaceous materials were filtered, washed with water and dried in an oven at 110 °C for 1 day. Fig. 3(a) shows the TEM image of the residual carbonaceous materials, in which no Si component was detected by EDX analysis (TEM: JEOL, JEM-2010; EDX: Oxford Link ISIS). A disordered mesoporous structure composed of mesopores (white regions) and nanothick carbon walls (dark regions) was observed in the extracted carbonaceous materials. The specific surface area and mean mesopore diameter of the carbonaceous materials, which were analyzed from N_2 adsorption isotherms (77 K) with BET and BJH methods (Micromeritics Gemini 2370), were 1065 $m^2\ g^{-1}$ and *ca.* 2.0 nm, respectively. When DVB monomer was directly introduced into mesopores of MCM-41 type MPS by an impregnation[8] and the composite was subjected to the treatments of heating in N_2 gas flow and aqueous HF solution, on the other hand, rod-like carbonaceous materials were obtained as shown in Fig. 3(b). Therefore, it can be concluded that the mesoporous carbonaceous material was obtained from the micelle/DVB/silicate precursor *via* the disordering of the composite nanostructure during the carbonization (heating) process.

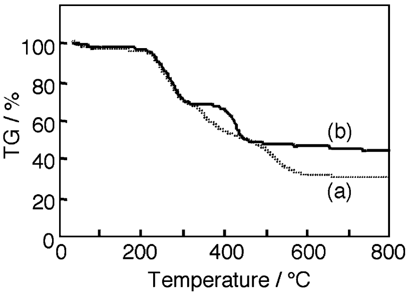

Fig. 2 Thermogravimetric curves of micelle/DVB/silicate composite; (a) in air, (b) in N_2 gas flow.

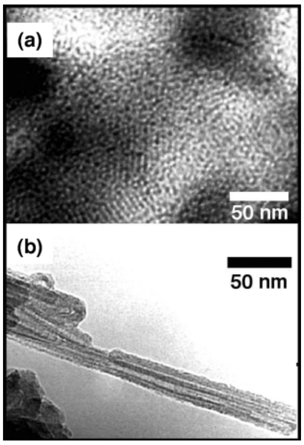

Fig. 3 TEM images of carbonaceous materials obtained after heating at 600 °C for 0.5 h (a) from micelle/DVB/silicate precursor and (b) by the impregnation method (see text).

A well-ordered mesoporous carbon was reported to be synthesized by the impregnation method which needs repetition of introduction of the carbon source into MCM-48 mesopores and heating.[9] Although a disordered porous carbon was obtained in the present study, the present method has potential as a time-saving synthetic process. Detailed investigations on the synthetic conditions are now in progress with the aim of obtaining ordered porous carbons. By removing the silicate from the polymer/micelle/silicate composite, the method is in principle applicable to the synthesis of morphologically controlled polymer/micelle nanomaterials.[10]

The study made use of instruments in the Center for Instruments Analysis (XRD, TEM) of Nagasaki University.

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