

## Template Synthesis of Nanoporous Carbons through Iodine Stabilization of Carboxymethylcellulose Sodium

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Iodine treatment before carbonization was applied to carboxymethylcellulose sodium to increase the char yield of carbons and to form NaI particles in the carbon matrix. A novel template synthesis of nanoporous carbons was achieved by removing NaI. The mechanism of this method was verified by the porosity and structure of the products obtained during the synthesis.

Template synthesis is one method to obtain porous carbons with precise structural design.<sup>1</sup> In typical methods for template synthesis, a composite of template and carbon is first synthesized, and then the template is removed to form pores. In general, templates and carbon sources are provided individually to form the composites, and many types of composites and combinations have been investigated.<sup>1–11</sup> Some inorganic templates with periodic structures have been known to have highly ordered, uniform, and even hierarchical porous structures. In other cases, methods to create both inorganic templates and carbons from one source are also well known. For example, defluorination of poly(tetrafluoroethylene) through reaction with alkali metals forms carbonaceous products and alkali fluoride particles, and then mesoporous carbons can be obtained by removing the fluoride particles by acid treatment.<sup>12,13</sup> It has also been reported that carbons including metal oxide template particles can be obtained immediately through the pyrolysis of organometallic materials. The particles in the carbons can be removed to produce pores.<sup>14,15</sup>

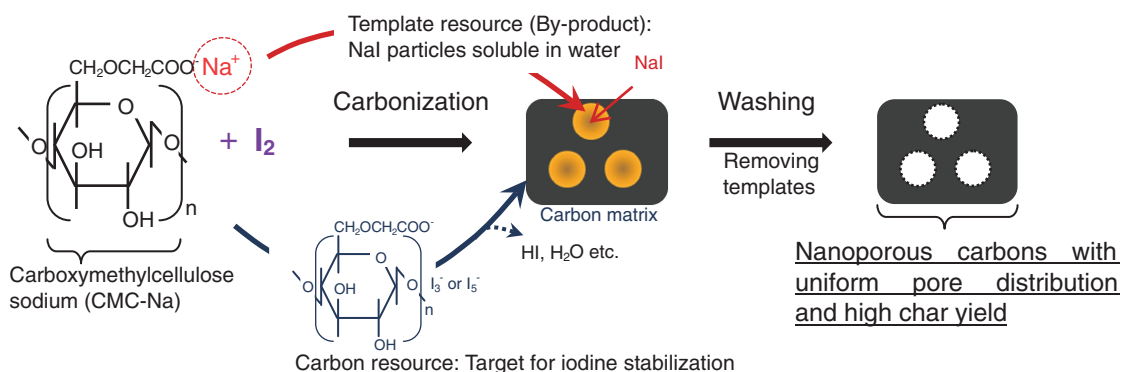
Thermal treatment with iodine vapor for organic precursors such as polymer and cellulose has received considerable attention as a method to increase the char yield of carbon after carbonization, it is known as a stabilization process.<sup>16–19</sup> This is because iodine can enhance radical polymerization of the

precursors by inducing a dehydrogenation reaction. Such polymerization prevents excessive weight loss by gasification in the carbonization process.

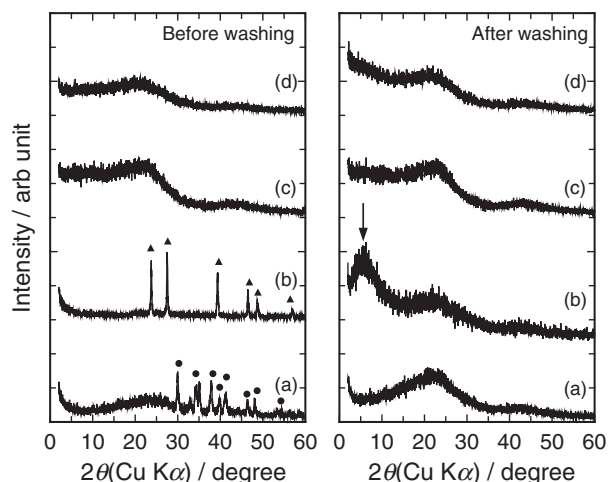
This study considers whether two chemical actions, i.e., iodine stabilization and production of alkali metal iodide particles, will occur if precursors including alkali metal atoms in the molecules react with iodine. The iodide particles will be dispersed in the stabilized precursors and remain after carbonization. Because alkali iodides are highly soluble in water and weak acid, a new route to produce porous carbons through the template carbonization synthesis is expected. This paper focuses on carboxymethylcellulose sodium (CMC-Na), which is a cellulose modified with  $-\text{CH}_2\text{COONa}$  groups in each molecular unit and widely used as a thickener in various fields. Iodine stabilization and carbonization of CMC-Na should simultaneously synthesize both template and carbon with high char yield and then result in novel nanoporous carbons by removing the template. The schematic illustration of the present mechanism is shown in Figure 1.

In this paper, structures and porosities of the products obtained by iodine treatment and carbonization of CMC-Na were characterized to verify the mechanism in Figure 1. For comparison, carboxymethylcellulose, CMC-H, which is modified with  $-\text{CH}_2\text{COOH}$  groups without sodium, was also used to discuss the creation and behavior of the expected inorganic NaI template.

CMC-Na (Wako Co., Ltd., Japan, Na content 6.5–8.5 mass %) or CMC-H (Gotoku Chemical Co., Ltd., Japan) was treated with iodine vapor at 115 °C for 3 h in a closed vessel in which CMCs and excess iodine solid were placed separately (I-CMC-Na and I-CMC-H). The reacted iodine content was evaluated from the weight of the resources after iodine treatment. Original CMCs and iodine-treated CMCs were carbonized at 600 °C in nitrogen flow (c-CMC-Na, c-CMC-H, c-I-CMC-Na,



**Figure 1.** Schematic representation of the present template synthesis of nanoporous carbons using CMC-Na and iodine.



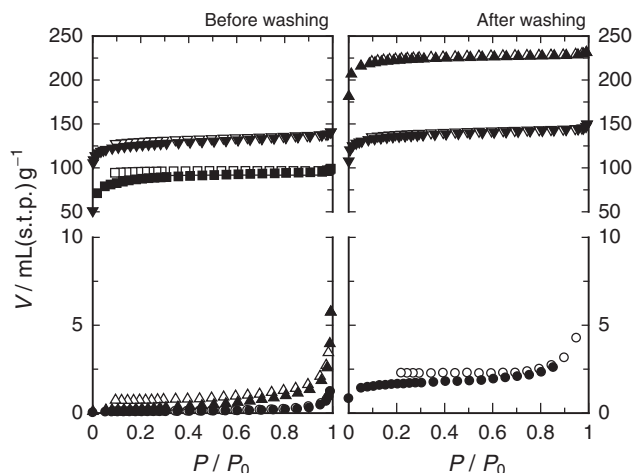
**Figure 2.** Changes of XRD patterns in carbons obtained before and after washing with deionized water. (a): c-CMC-Na, (b) c-I-CMC-Na, (c) c-CMC-H, (d) c-I-CMC-H. ●:  $\text{Na}_2\text{CO}_3$ , ▲: NaI. The arrow indicates 1.8 nm periodicity in c-I-CMC-Na.

and c-I-CMC-H). The heating rate was  $10^\circ\text{C min}^{-1}$  and the retention time was 1 h. After carbonization, original CMCs and iodine-treated CMCs were immersed and filtered in deionized water several times to remove inorganic by-products from the carbon matrix. The char yield of carbons was evaluated from the weight loss of the carbonized samples after washing. The structures and porosities of the carbonized samples before and after washing were characterized by X-ray diffraction (RINT Ultima<sup>+</sup>, Rigaku) and nitrogen gas adsorption at  $-196^\circ\text{C}$  using a volumetric apparatus (BELSORP-mini, Bel Japan Inc.), respectively. The samples were preheated at  $300^\circ\text{C}$  in argon flow before the adsorption measurement.

The CMC samples after iodine treatment changed color uniformly from white to deep blue, which reveals they were well stabilized by iodine. The iodine contents in I-CMC-Na and I-CMC-H were ca. 32 and 30 mass %, respectively. This implies that the reactivity of the two CMCs with iodine is almost the same.

Figure 2 shows the changes in XRD patterns of c-CMCs before and after washing with deionized water. The pattern of c-CMC-H shows almost no changes after washing. Only (002) broad peaks of amorphous carbon at around  $25^\circ$  were observed. This indicates that no inorganic by-product template is created. On the other hand, strong peaks corresponding to NaI are detected in the pattern of c-I-CMC-Na, while those corresponding to  $\text{Na}_2\text{CO}_3$  are detected in the pattern of c-CMC-Na. As shown in the right panel of Figure 2, both sodium salts disappear completely after washing with water, and only the patterns of carbon remain. Note that a new broad peak appeared at around  $5^\circ$  in c-I-CMC-Na after washing (arrow in Figure 2). Such a peak is not observed in other samples. This peak can be assigned to the particular periodic structure of carbons because other peaks for NaI disappeared. The estimated  $d$  value is around 1.8 nm, which corresponds to the formation of micropores with relatively uniform pore size, resulting from the removal of NaI from the carbon matrix.

Figure 3 shows nitrogen adsorption isotherms at  $-196^\circ\text{C}$  of c-CMCs before and after washing with water. c-CMC-H and c-I-



**Figure 3.** Changes in nitrogen adsorption/desorption isotherms at  $-196^\circ\text{C}$  for carbons obtained before and after washing by deionized water. Closed marks: adsorption branch, Open marks: desorption branch. ●: c-CMC-Na, ▲: c-I-CMC-Na, ■: c-CMC-H, ▼: c-I-CMC-H.

**Table 1.** Specific surface area and char yield at  $600^\circ\text{C}$  for carbonized samples

Sample	Char yield /mass %	Surface area/ $\text{m}^2 \text{g}^{-1}$	
		before washing	after washing
c-CMC-Na	17	2	5
c-I-CMC-Na	22	2	1070
c-CMC-H	24	350	—
c-I-CMC-H	29	600	600

CMC-H before washing show type I isotherms in IUPAC classification, indicating that they are microporous carbons. The micropores for c-I-CMC-H are more developed than those for c-CMC-H because of higher nitrogen adsorption of c-I-CMC-H at  $P/P_0 \approx 0$ . This indicates that iodine stabilization effectively enhances the microporosity of the present CMC material. Such an effect of iodine on cellulose-based materials has been previously reported,<sup>17,18</sup> and the present results are in good accordance with these previous results.

The isotherms of c-CMC-Na and c-I-CMC-Na show a considerably small amount of nitrogen adsorption because the two samples include a significant amount of inorganic sodium salts, as shown in their XRD patterns. After washing with water, the isotherms of c-I-CMC-H are not markedly changed. In contrast, the isotherms of c-I-CMC-Na changes from type II to type I after washing, which suggests that the micropore volume increased through the removal of inorganic materials. The amount of nitrogen adsorption is significantly larger for c-I-CMC-Na than for c-CMC-Na.

Specific surface areas of the samples calculated from those isotherms by  $\alpha_s$  plot,<sup>20</sup> which can be used to evaluate micropores of pore width smaller than 2 nm, are summarized in Table 1 along with their char yield at  $600^\circ\text{C}$ . To compare the difference in surface areas for carbons before and after removing the template, the surface areas of c-CMC-Na and c-I-CMC-Na

before washing were calculated using only the mass of corresponding carbons after washing. The micropores are not considerably developed by direct carbonization of CMC-Na and the following removal of  $\text{Na}_2\text{CO}_3$ . This inorganic by-product particle cannot function as a template in this carbonization condition. On the other hand, washed c-I-CMC-Na shows significant development micropores, which reveals that the effect of removal of the NaI particles from the carbon matrix facilitates its use as a template. The surface area of washed c-I-CMC-Na is considerably higher than that of c-I-CMC-H. It is presumed that NaI begins to form and is dispersed in the polymer structure during the iodine stabilization process;  $\text{Na}_2\text{CO}_3$  does so only during the carbonization process. This may contribute to the difference in the template effect between c-CMC-Na and c-I-CMC-Na.

As previously mentioned, washed c-I-CMC-Na has a peculiar diffraction peak at  $5^\circ$  in its XRD pattern. This suggests that relatively uniform micropores are formed. The peak is due to the periodic distance of 1.8 nm and does not correspond directly to the pore size because the distance includes the thickness of carbon walls around the pores. Therefore, a narrow micropore size distribution of less than 1.8 nm is expected from the XRD results. NaI particle size estimated by XRD pattern, however, does not correspond to pore size formed by removing NaI. This implies that every NaI particles do not behave as templates. It is considered that some NaI particles aggregate on the carbon matrix surface as well as disperse uniformly in the matrix. The NaI particles on the matrix will grow larger than those in the matrix during carbonization. Therefore, such aggregated NaI must be mainly detected as the sharp peak in the XRD patterns. TEM observation has been attempted to clarify the NaI particle size; however it has not yet obtained convincing evidence. Since the higher angle diffraction pattern than the observed peak at  $5^\circ$  in washed c-I-CMC-Na, it is also suggested that the periodicity of micropore arrangement is not high enough to determine lattice symmetry. The narrow distribution is a very notable characteristic and will be studied more in detail with other characterization techniques.

The char yield of both c-I-CMC-H and c-I-CMC-Na is slightly higher than c-CMC-H and c-CMC-Na. In addition, for the materials in the present study, the iodine stabilization is effective to promote polymerization, as previously reported for other cellulose materials.<sup>17,18</sup>

It is concluded that iodine treatment of pristine CMC-Na results in two actions: stabilization effect of increasing char yield and formation of NaI template particles in the carbon matrix. By removing the NaI template, a specific surface area of over  $1000 \text{ m}^2 \text{ g}^{-1}$  was achieved. The template method using iodine stabilization was successfully demonstrated to be a novel template synthesis of nanoporous carbons from cellulose-based

materials. The advantages of this iodine treatment were (1) simultaneous development of porosity and increased char yield, (2) creation of an inorganic template from only one source, and (3) superior pore size uniformity.

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