Formation mechanism of zeolite-templated carbons

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The formation mechanism of zeolite-templated carbons (ZTCs) is investigated. The carbon uptake into zeolite nanochannels during chemical vapor deposition (CVD) is found to proceed in the following three stages: (i) initial rapid carbon uptake from zeolite-particle surface to its center, (ii) gradual increase of carbon density at a constant rate, and (iii) termination of carbon deposition. The molecular-level structure evolution is also analyzed in detail. By CVD, curved nanographenes are formed inside the nanochannels of zeolite, and they are not perfectly connected each other. The subsequent heat treatment ($>800\text{ }^{\circ}\text{C}$) coalesces the nanographenes to form a continuous 3D framework, and at the same time, a significant number of dangling bonds (non-terminated edge sites) are formed that are protected from air by the zeolite so that they are stable at room temperature. However on template removal, the dangling bonds react with ambient H_2O or O_2 and are terminated by oxygen-functional groups or H. The dangling bonds in the carbon/zeolite composite can also be terminated by H when the composite is subjected to a H_2 treatment at $700\text{ }^{\circ}\text{C}$. In this case, the number of dangling bonds in the carbon/zeolite composite is decreased, and the addition of oxygen-functional groups when the template is removed becomes less significant.

KEYWORDS : Zeolite-templated carbons, Graphene, Porous carbons, Chemical vapor deposition, Dangling bonds

1. Introduction

Zeolite-templated carbons (ZTCs) are ordered microporous carbons that are synthesized in the confined nanospace of zeolite templates¹⁾⁻⁵⁾. **Fig. 1** shows a possible structure model which we have previously proposed⁶⁾. ZTC consists of curved and non-stacked nanographenes constructing a 3D ordered framework⁶⁾, and has a significant amount of graphene edge sites terminated by hydrogen or oxygen-functional groups⁷⁾. ZTC thus possesses unique spin/magnetic properties⁸⁾ and is predicted to have a unique band structure⁹⁾. Moreover, ZTCs possess long-range structure regularity derived from zeolites²⁾ and a developed microporosity (BET surface area is $2000\sim4000\text{ m}^2/\text{g}$, and micropore volume is $1.0\sim1.8\text{ cm}^3/\text{g}$)¹⁰⁾. These unique properties make ZTCs attractive candidates for a variety of applications, including hydrogen storage^{11),12)}, fuel cells¹³⁾, electrochemical capacitors¹⁴⁾⁻¹⁶⁾, catalysts^{17),18)}, and catalyst supports^{19),20)}.

Another advantage of ZTCs is chemical controllability. It is possible to introduce heteroatoms, such as $\text{N}^{21)}$, $\text{B}^{22)}$, and $\text{S}^{18)}$, into the framework of ZTCs, and it is also possible to chemically modify a large amount of active edge sites by post-synthesis methods^{7),23),24)}. Such chemical modifications expand the possibility of ZTCs towards

versatile functional materials for demanded applications. However, the details of the formation mechanism of ZTCs have still not been understood very well, and it is highly desired to have deeper insight for much more precise chemical design of the ZTC frameworks. In this work, we report detail formation mechanisms of ZTC frameworks, specifically about the following two matters: (i) carbon-filling process during chemical-vapor deposition (CVD) and (ii) molecular-level framework evolution.

Fig. 1 (Color online) Structure model of ZTC. Carbon, hydrogen, and oxygen atoms are represented by black, blue, and red spheres, respectively.

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Fig. 2 (Color online) Schematic for sample preparation: (a) Zeolite Y. A bottom image shows a supercage and its window (d_w) and inner-pore (d_s) sizes estimated by considering van der Waals radius of pore walls. (b ~ g) A series of samples prepared. Si-O-Si bonds in zeolite Y are drawn by blue lines, while the carbon framework is simply represented by thick lines. Note that (e) corresponds to the framework morphology of the molecular-level structure shown in Fig. 1.

2. Methods

2.1 Analysis of carbon filling process during CVD

Zeolite X (Na-type Faujasite, Union Showa K. K., 13X) with a large particle size (*ca.* 1 ~ 2 μm) was used as a template¹⁴⁾. Specifically, well-dried zeolite X (0.5 g) was heated up to 600 °C in a N_2 flow, and then mixture gas of 15-vol%-acetylene/ N_2 was fed for CVD during a designed period (t_{CVD} =0.25, 0.5, 1, 2, 4, or 8 h). The sample was further heat-treated at 850 °C in a N_2 flow for 3 h. A heating rate was always 5 °C/min. The amount of carbon loaded onto the zeolite template (W_{TG} [g-carbon/g-zeolite]) was calculated from the weight loss when the sample was heated up to 800 °C in a thermogravimetric analyzer (Shimadzu TGA-51H) under an air flow. Moreover, the carbon/zeolite composite was washed with hydrofluoric acid (HF) to liberate ZTC for the observation on a transmission electron microscope (TEM; JEM-2010, JEOL Ltd.).

2.2 Analysis of molecular-level framework evolution

To elucidate the structure evolution by CVD, heat treatment (HT), and HF treatment, a series of samples was synthesized by the scheme illustrated in **Fig. 2**. Zeolite Y (Na-type Faujasite, Tosoh, HSZ-320NAA, particle size is *ca.* 200 nm), was used as a template (**Fig. 2a**). Note that the procedure shown in **Figs. 2a, b, d, and e** is a typical scheme for obtaining ZTC by the CVD method²⁵⁾. Other samples are intermediates or references to understand the framework evolution. The synthesis procedure is basically the same as that described in the section 2.1, except for an acetylene concentration (5 vol%) for CVD and a heat treatment temperature (900 °C) after CVD. The sample names are all shown in **Fig. 2**.

Precise elemental analysis of carbon frameworks was carried out by temperature-programmed oxidation (TPO)⁶⁾. From W_{TG} and the CHO ratio, an average $\text{C}_n\text{H}_m\text{O}_l$ formula of a unit structure corresponding to one zeolite supercage was determined⁶⁾. The liberated

carbons were characterized by Raman spectroscopy, X-ray diffraction (XRD), and N_2 adsorption/desorption measurement. Raman spectra were measured with a micro-Raman apparatus with 488.0 nm line⁶⁾. The intensity was normalized by the G-band. Powder XRD patterns of the samples were recorded with an X-ray diffractometer (Shimadzu, XRD-6100) with $\text{Cu K}\alpha$ radiation. Nitrogen physisorption measurements were carried out at -196 °C on a BELSORP Mini apparatus (BEL Japan). Brunauer-Emmett-Teller (BET) surface area was calculated using an adsorption isotherm in the range of P/P_0 =0.01 ~ 0.05 to avoid the overestimation in microporous carbons²⁶⁾. Magnetic susceptibility data were collected in the temperature range of 2 to 300 K in an applied field of 10 kG using a SQUID magnetometer (Quantum Design MPMS5). The samples were thoroughly evacuated, and subjected to the measurement in a closed vessel to avoid the effects of adsorbed species. The magnetic susceptibility data were fitted with the Curie-Weiss model with a temperature-independent term. The spin density is calculated from the Curie-constant.

Molecular-level structure models were constructed for carbon/zeolite composites and ZTCs. According to $\text{C}_n\text{H}_m\text{O}_l$, the model previously reported⁶⁾ (**Fig. 1**) was modified to construct primitive models, and they were subjected to structure optimization by using the FORESITE algorism with the COMPASS II force field available in the BIOVIA Materials Studio 2017. For Y-Ac6(4)Z and Y-Ac6(4)-H9(3)Z, the optimization calculations were carried out in the presence of zeolite framework. In each case, periodic boundary condition was applied.

3. Results and Discussion

3.1 Analysis of carbon filling process during CVD

Fig. 3 shows the increase of W_{TG} against CVD period (t_{CVD}). The weight loss by HT is usually less than 10%, and W_{TG} reflects the amount of carbon introduced by CVD. The CVD process can be di-

Fig. 3 (a) The relation between W_{TG} and t_{CVD} . Three stages are defined in $t_{CVD} < 0.5$ h (Stage I), $0.5 \text{ h} < t_{CVD} < 5.8$ h (Stage II), and $t_{CVD} > 5.8$ h (Stage III). A solid linear line is an approximate line of the plots for $t_{CVD} = 0.5, 1, 2$, and 4 . A horizontal dashed line expresses the maximum W_{TG} (0.32 g/g). (b ~ e) TEM images of liberated carbons ($t_{CVD} = 0.25, 2, 4$, and 8 h). Scale bars are $1 \mu\text{m}$.

Fig. 4 Schematic of carbon-filling process in zeolite by CVD. (a) A zeolite particle before CVD. (b ~ d) The states corresponding to Stage I, II, and III, respectively.

vided into three stages. In the initial Stage I, carbon is very quickly introduced into empty zeolite pores. Then in Stage II, the weight increase becomes less intense because zeolite pores are narrowed by the carbon deposition, and W_{TG} is increased in proportion to t_{CVD} . At the CVD temperature of 600°C , acetylene is not decomposed in a gas phase but converted into carbon only with the catalysis of zeolite. Therefore, when active sites of zeolite are fully covered by carbon, carbon deposition is terminated. This is Stage III. Indeed at $t_{CVD} = 8$ h, the carbon loading amount (0.32 g/g , $24.4 \text{ wt\%}$) becomes lower than the amount that can be extrapolated from the approximate line in the Stage II. From the approximate line in the Stage II, it is possible to estimate that Stage II is finished at $t_{CVD} = 5.8$ h.

Figs. 3b~e show TEM images of liberated carbons. **Fig. 3b** shows a hollow space, meaning that the carbon deposition takes place gradiently from the outside surfaces of zeolite particles toward their centers. Here, a net carbon-loading amount ($W_{net} [\text{g/g}]$) is defined as a carbon-loading amount only in the carbon-reached region in zeolite particles. W_{net} can be calculated by $W_{net} = W_{TG} / \phi_C$, where ϕ_C is the volume ratio of the carbon-filled region in a carbon/zeolite composite. For example, if carbon is introduced only in the zeolite channels near the outside surface, W_{net} is much larger than W_{TG} ($W_{net} > W_{TG}$). When carbon is homogeneously introduced in a whole zeolite particle, W_{net}

becomes W_{TG} ($W_{net} = W_{TG}$). From **Fig. 3b**, ϕ_C at $t_{CVD} = 0.25$ h can be estimated as 0.93 , yielding $W_{net} = 0.24 \text{ g/g}$, slightly larger than W_{TG} (0.22 g/g). Though **Fig. 3b** shows a noticeable void in the core of a particle, its volume ratio is actually very small (0.07), and thus W_{net} is not greatly larger than W_{TG} . In **Fig. 3c**, there are still small crack-like spaces, but the carbon deposition reaches almost the center of a zeolite particle, *i.e.*, $\phi_C \approx 1$. In **Figs. 3d** and **e** ($t_{CVD} > 4$ h), ZTC particles look homogeneous, indicating that zeolite particles are fully infiltrated with carbon ($\phi_C = 1$, and therefore $W_{net} = W_{TG}$).

From the results obtained, carbon filling process can be summarized as shown in **Fig. 4**. In Stage I, empty zeolite pores (**Fig. 4a**) are rapidly infiltrated by a low-density carbon (**Fig. 4b**) from the outside of zeolite particles toward their centers. Then in Stage II (**Fig. 4c**), W_{net} ($\approx W_{TG}$) is slowly increased at a constant rate. Increase of W_{net} means the increase of the number of carbon atoms introduced per one supercage. At the same time, a small portion of empty zeolite pores would be filled with carbon. Stage III is the period after W_{net} reaches the maximum (0.32 g/g) at which the carbon deposition is terminated (**Fig. 4d**). Note that the maximum W_{net} value could slightly differ depending on the types of carbon source and zeolite template, and also on some CVD conditions. Nevertheless, the basic behavior proposed in **Fig. 4** should be generalized, as far as CVD is performed below

Table 1 Properties of a series of carbon/zeolite composites and ZTCs shown in Fig. 2.

Sample	W_{TG} (g/g)	Elemental analysis (wt%) ^a			H/C (mol/mol)	$C_nH_mO_l$ ^b	S_{BET} (m ² /g)
		C	H	O			
Y-Ac6(4)Z	0.38	97.8	2.1	0.1	0.26	C ₄₉ H ₁₃	n/a ^c
Y-Ac6(4)	n/a	n.d. ^d	n.d.	n.d.	n.d.	n.d.	960
Y-Ac6(4)-H9(3)Z	0.35	99.3	0.6	0.1	0.072	C ₄₅ H ₃	n/a
Y-Ac6(4)-H9(3)	n/a	93.0	1.0	6.0	0.13	C ₄₅ H ₆ O ₂	2680
Y-Ac6(4)-H9(3)-Hyd7(2)Z	0.34	99.2	0.7	0.1	0.084	C ₄₅ H ₄	n/a
Y-Ac6(4)-H9(3)-Hyd7(2)	n/a	96.4	1.1	2.5	0.14	C ₄₅ H ₆ O	2800

^aCHO ratio determined by TPO. ^bAverage $C_nH_mO_l$ formula corresponding to the unit structure included in one zeolite supercage. ^cn/a: Not applicable. Carbon/zeolite composites show almost no N₂ adsorption. W_{TG} cannot be defined for ZTCs. ^dn.d.: No data.

Fig. 5 (a) Raman spectra, (b) XRD patterns, and (c) N₂ adsorption/desorption isotherms of Y-Ac6(4) and Y-Ac6(4)-H9(3). For (b), an XRD pattern of zeolite Y is also shown. In (c), solid and blank circles correspond to adsorption and desorption data, respectively.

the temperature of non-catalytic carbonization of CVD-source gas.

3.2 Analysis of molecular-level framework evolution

Table 1 summarizes W_{TG} , CHO ratio, H/C ratio, $C_nH_mO_l$, and BET surface area for each sample prepared by the scheme shown in **Fig. 2**. By acetylene CVD at 600 °C, 0.38 g/g (27.6 wt%) of carbon is introduced into zeolite, and the building unit is C₄₉H₁₃ (**Table 1**). The carbon content is then slightly decreased to 0.35 g/g (25.7 wt%) by the subsequent HT at 900 °C, and the building unit is changed into C₄₅H₃. The morphologies of the carbons in zeolite nanochannels can be indirectly understood from the characterization results on the corresponding liberated carbons (**Fig. 5**). The Raman spectra of Y-Ac6(4) and Y-Ac6(4)-H9(3) are almost the same (**Fig. 5a**). This indicates that Y-Ac6(4) has a similar structure feature to that of Y-Ac6(4)-H9(3), *i.e.*, curved single-layer nanographene like **Fig. 1**⁶⁾. Note that the present CVD condition forms negligible outside pyrocarbon shells on zeolite particles¹⁵⁾, and the Raman spectra represent the carbon structures formed inside the zeolite nanochannels. However, Y-Ac6(4) does not have a sharp XRD peak at $2\theta=6.4^\circ$ corresponding to zeolite (111) planes unlike Y-Ac6(4)-H9(3) (**Fig. 5b**). In addition, Y-Ac6(4) shows a broad carbon (002) peak. The XRD results indicate that the nanographenes in Y-Ac6(4)Z are not fully connected each other and cannot retain the ordered structure when the template is removed, as illustrated in **Fig. 2c**. Such framework collapse would give rise to the stacking of nanographenes (carbon (002) peak in

Fig. 5b), resulting in the decline of porosity²⁷⁾ as found in **Fig. 5c**. Considering these findings, the molecular-level carbon structures formed in zeolite nanochannels before and after HT can be illustrated in **Figs. 6a** and **b**, respectively. Simply from the C₄₉H₁₃ formula in Y-Ac6(4)Z, we can assume the curved nanographene structure rather than a planer structure because of the following two reasons: (i) The H/C ratio is too small to assume a planer nanographene structure. (ii) The planer nanographene containing 49 of carbons is too big to exist inside the supercage (**Fig. 2a**). By HT, discrete nanographenes should be coalesced to form a continuous robust framework which can stand even after template removal. At the same time, the original H/C ratio (0.26) is greatly decreased to 0.072 (**Table 1**). Though some amount of edge sites are lost by the coalescence, the amount of H (0.072) is still too small to terminate all of the edges sites of the 3D nanographene framework. Hence, the framework should have a lot of dangling bonds (**Fig. 6b**), *i.e.*, σ -radicals. Though dangling bonds are generally not stable under atmosphere, zeolite could protect them from air.

Next, the structure change by the HF treatment is discussed. From Y-Ac6(4)-H9(3)Z to Y-Ac6(4)-H9(3), the unit structure is changed from C₄₅H₃ to C₄₅H₆O₂. The increase of H and O indicates that the dangling bonds which were protected by zeolite in Y-Ac6(4)-H9(3)Z react with H₂O or O₂ and are terminated by oxygen-functional groups or H upon the HF treatment. Hence, the origin of oxygen in

Fig. 6 (Color online) Molecular-level structural models for each of synthesis steps: (a) Y-Ac6(4)Z, (b) Y-Ac6(4)-H9(3)Z, (c) Y-Ac6(4)-H9(3), and (d) Y-Ac6(4)-H9(3)-H9(3)-H9(3)-H9(3).

ZTC framework should be H_2O or O_2 , *i.e.*, environmental species. A molecular-level structure for Y-Ac6(4)-H9(3) is thus illustrated in **Fig. 6c**. We then tried to characterize the presence of dangling bonds (σ -radical) in Y-Ac6(4)-H9(3)Z. Zeolite Y has a spin density of $50 \mu\text{mol/g}$, which can be ascribed to a very small amount of impurities, and the amount of spin included in one supercage is calculated to be 0.079 on average. The localized spin density in Y-Ac6(4)-H9(3)Z is $95 \mu\text{mol/g}$. Considering the effect of zeolite, the amount of spin in one building unit of carbon framework is calculated to be 0.12 on average. This is much smaller than the number of dangling bonds (3 per one unit) included in the presumed molecular-level structure (**Fig. 6b**). This could be due to hybridization between σ -radical states of carbon electron orbitals and the substrate (zeolite). Guo *et al.* have indeed reported the disappearance of the spin-polarized edge sites in zigzag graphene nanoribbons supported on Si or SiO_2 substrate^(28),29). Though the direct detection of dangling bonds (σ -radical) in Y-Ac6(4)-H9(3)Z is found to be difficult because of their hybridization with zeolite, the precise elemental analysis strongly suggests the presence of dangling bonds as described above. By template removal with HF, most of dangling bonds should immediately react with H_2O or O_2 , because the ZTC framework has a fully open porous network and the entire surface is exposed to HF solution or air. Indeed, Y-Ac6(4)-H9(3) has a spin density of $170 \mu\text{mol/g}$, corresponding to only 0.10 of spin per one unit structure. Since it is possible to assume that dangling bonds (σ -radical) are mostly terminated, the small amount of remaining spin could be ascribed to H-terminated zigzag edge sites (π -radical)⁽³⁰⁾. Some of them could be formed by CVD, and some others could be formed by the termination reaction upon HF treatment.

The activity of σ -radical in Y-Ac6(4)-H9(3)Z was examined by

a H_2 treatment at 700°C . The resulting Y-Ac6(4)-H9(3)-H9(3)-H9(3)-H9(3) shows an increase of H content as well as H/C ratio (**Table 1**), and the unit structure becomes C_{45}H_4 which has one additional H compared to its precursor (C_{45}H_3). Interestingly, the unit structure of the liberated carbon is $\text{C}_{45}\text{H}_6\text{O}$ (**Fig. 6d**), which has one-less number of oxygen than that in Y-Ac6(4)-H9(3) ($\text{C}_{45}\text{H}_6\text{O}_2$). These results demonstrate that the dangling bonds of the carbon framework in zeolite can be end-capped by hydrogen, and such a treatment can avoid the addition of oxygen-functional groups upon the HF treatment. The decrease of the oxygen amount means that the framework of Y-Ac6(4)-H9(3) becomes lighter in Y-Ac6(4)-H9(3)-H9(3)-H9(3)-H9(3). Thus, the surface area of the former ($2680 \text{ m}^2/\text{g}$) is estimated to increase to $2756 \text{ m}^2/\text{g}$ simply by the weight change of the framework. Indeed, the surface area is increased to $2800 \text{ m}^2/\text{g}$ (**Table 1**), a very close value to the estimated one. The results of H_2 -treated samples further support the mechanism shown in **Figs. 6a~c**.

4. Conclusion

The formation mechanism of ZTC is investigated in detail. The carbon filling process into zeolite by CVD is found to be divided into three stages: (i) rapid carbon uptake into blank zeolite nanochannels from the zeolite-particle surface into its center, (ii) gradual increase of carbon density at a constant rate, and (iii) termination of carbon filling. The molecular-level structure evolution during the synthesis process of ZTC is also analyzed. CVD forms curved nanographenes which are not perfectly connected each other inside zeolite nanochannels. Subsequent HT makes the nanographenes coalesce to form a continuous 3D framework having a significant amount of dangling bonds (non-terminated edge sites). When template is removed by HF, the dangling bonds react with water and/or air, and the edge sites

are finally terminated by H and oxygen-functional groups. It is also found that an end-capping of the dangling bonds is possible by H₂ treatment of carbon/zeolite composite. ZTC thus obtained has much less amount of oxygen-functional groups than that without the H₂ treatment. This work thus revealed new insights into the ZTC formation process, and the findings obtained would facilitate the development of new functional carbon materials based on ZTC.

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