# Graphitic Porous Carbons Prepared by a Modified Template Method

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Graphitic porous carbons were prepared by adding $FeCl_3$ into a preliminary water-soluble mixture of poly(vinyl alcohol) and magnesium acetate, followed by carbonization and acid washing. The samples were then characterized by X-ray diffraction (XRD) and $N_2$ adsorption at 77 K. XRD patterns showed that Fe could accelerate carbon graphitization at 1000 °C. Although the MgO particles worked as template, they resulted in the decrease of crystallinity. Thus it is necessary to balance between crystallinity and pore structures for diversified applications.

Porous carbon has drawn a lot of attention owing to its emergent application to energy storage in supercapacitors. Furthermore, the use of carbon black and some novel forms of carbons including ordered porous carbon, carbon nanotubes, and carbon aerogel as catalyst supports in fuel cells has also aroused great interest. Most of them have poor electroconductivity except carbon nanotubes. Recently, several scientists have focused their research on the fabrication of graphitic porous carbons. These carbons have better electrical conductivity due to their crystalline nanostructure. The conventional method requires very high temperature (>2000 °C) to graphitize the carbon framework.[1,2] It is necessary to develop a new approach with lower energy consumption. It has been known that in the presence of certain transition metals (Fe, Co, Ni, etc.), the carbon framework can be changed into graphitic structure at relatively low temperature. Several attempts have been made successfully in this way.[3–6]

Recently, a facile template method was developed to prepare porous carbons using thermoplastic precursors and MgO.[7–10] In the present work we use a simply modified template method to prepare graphitic porous carbons, in which $FeCl_3$ is added to catalyze graphitization during carbonization.

The graphitic porous carbon was prepared as follows: The carbon precursor, 5 g of poly(vinyl alcohol) (PVA), was dissolved in 50 mL of water under stirring at 90 °C, then mixed with $Mg(CH_3COO)_2$ at various ratios: PVA/MgO = 7/3, 6/4, 5/5, and 3/7. The PVA/MgO ratio was calculated on the basis of the mass of MgO. 2.54 g of $FeCl_3$ was then added to the solution. After drying, the mixture was heated up to 1000 °C in $N_2$ for 3 h at a rate of 5 °C/min. Finally, the material was washed with 10% HCl to remove MgO and catalyst particles. These samples were labeled as $a/b$-$x$ ($a/b$ = mass ratio of PVA/MgO, $x$ = heat treatment temperature). Samples derived from PVA mixed with $FeCl_3$ or $Mg(CH_3COO)_2$ only were named as Fe-1000 and 5/5Mg-1000. X-ray diffraction (XRD) patterns were recorded on a D8 Advance diffractmeter with Cu K$\alpha$ radiation. $N_2$ adsorption–desorption isotherms were measured at 77 K with an ASAP2010 adsorption analyzer. Transmission electron microscopy (TEM) images were obtained with a JEOL 2100F microscope, the acceleration voltage was 200 kV.

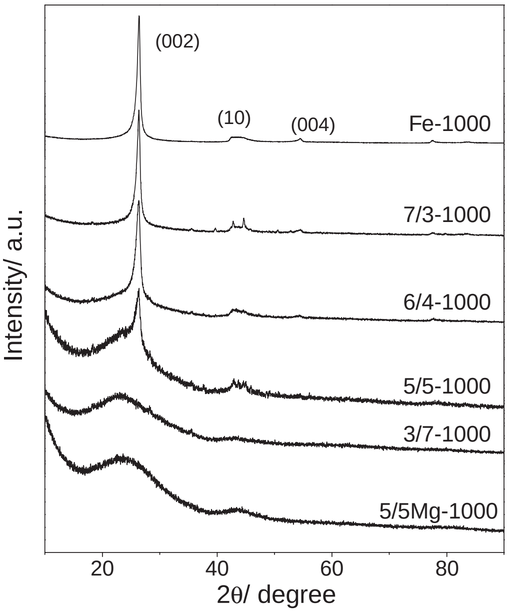

**Figure 1.** XRD patterns for resultant carbons after Fe and MgO removal.

During carbonization, $Mg(CH_3COO)_2$ was pyrolyzed to give nanosized particles of MgO below 200 °C. At higher temperatures, plasticized PVA coated onto MgO particles and then carbonized as thin layer.[10] Pore structure can be obtained after MgO template is dissolved by HCl. Figure 1 illustrates a series of powder XRD patterns of resultant carbons obtained from various precursors. The crystallinity of the resultants varied remarkably, depending on their PVA/MgO mass ratios, while the PVA/$Fe_2O_3$ mass ratio was held at 4/1 (2.54 g of $FeCl_3$) for all samples.[10] XRD patterns (figure not shown) confirmed the existence of $\alpha$-Fe and MgO. The Fe ions were reduced into $\alpha$-Fe particles, which may catalyze the graphitization by dissolution–precipitation of carbon atoms. Although Fe-1000, 7/3-1000, and 6/4-1000 all have very sharp 002 peaks, peaks of 100 or 101 cannot be observed clearly. It could be concluded that these carbons are two-dimensionally ordered structure (turbostratic structure) rather than graphite structure with ABAB··· stacking regularity. For 5/5-1000, the 002 peak emerging from the amorphous profile indicated that only part of the carbon had changed into turbostratic structure. And for 3/7-1000, the carbon remains entirely amorphous after heat treatment, showing that the large amount of MgO weakened the activity of Fe catalyst.

Figure 2 displays the TEM image of the graphitic porous carbons. For 5/5-1000, a large number of spherical pores with wall thicknesses of less than 10 nm can be found (Figure 2a). Furthermore, the high-resolution transmission electron microscopy (HRTEM) image (Figure 2b) proved the carbon framework possessed a random nanotexture, which is consistent with the

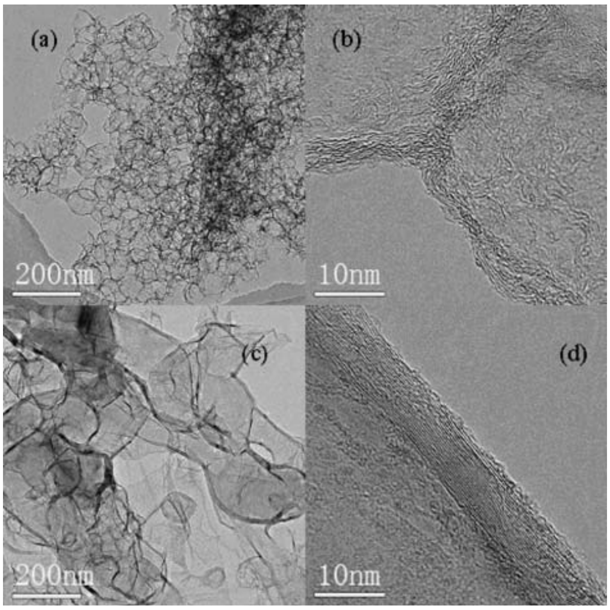

**Figure 2.** TEM and HRTEM images of porous graphitic carbons: (a) 5/5-1000; (b) HRTEM image of 5/5-1000; (c) 7/3-1000; (d) HRTEM image of 7/3-1000, 002 lattice image.

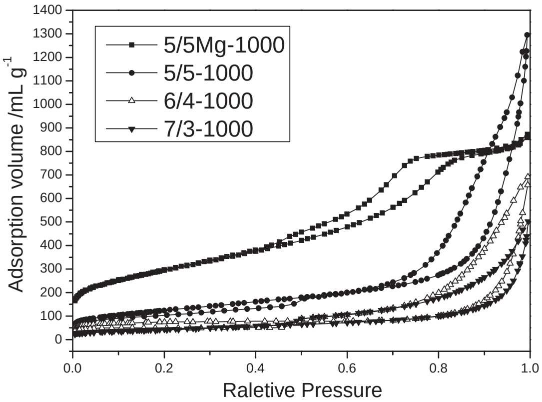

**Figure 3.** $N_2$ adsorption–desorption isotherms of resultant carbons.

XRD result. As shown in Figure 2c, pore size is larger in 7/3-1000. Pore walls were composed of graphitic ribbons, and a lattice image can be clearly observed with HRTEM (Figure 2d).

**Table 1.** Parameters from nitrogen adsorption

| Sample | $S_{\mathrm{BET}}$ /m$^2$ g$^{-1}$ | $V_{\mathrm{tot}}{}^{a}$ /cm$^3$ g$^{-1}$ | $\overline{D}^{b}$ /nm |
|---|---|---|---|
| 5/5Mg-1000 | 1059 | 1.350 | 5.10 |
| 5/5-1000 | 451 | 2.000 | 17.7 |
| 6/4-1000 | 260 | 1.016 | 15.6 |
| 7/3-1000 | 158 | 0.778 | 19.7 |
| Fe-1000 | 76 | 0.316 | 16.6 |

$^{a}V_{\mathrm{tot}}$, total pore volume obtained at $p/p_0 = 0.995$. $^{b}\overline{D}$, calculated by $4V/S_{\mathrm{BET}}$.

Figure 3 shows $N_2$ adsorption–desorption isotherms of samples, and the pore structure parameters are listed in Table 1. The isotherm of 5/5Mg-1000 is type IV, indicating the ability of MgO to produce mesopores. But some micropores also exist since the carbon layer on MgO is believed to be microporous.[10] Other isotherms of graphitic porous carbons exhibited little adsorption at low relative pressures but significant adsorption with obvious hysteresis loops at high relative pressures, revealing the characteristics of meso- and macroporous structures.

Without catalyst, 5/5Mg-1000 can reach a specific surface area of more than 1000 m$^2$/g. However, for 5/5-1000, the micropores were partly eliminated during graphitization, the specific surface area decreased remarkably to 451 m$^2$/g while the pore volume increased to 2,000 cm$^3$/g. Moreover, this catalytic effect was strengthened as the proportion of MgO decreased, resulting in decrease in both surface area and pore volume. As expected, Fe-1000 shows the lowest specific surface area and pore volume for there was no MgO template existed. It could be attributed to the following two factors: first, a lower amount of template creates fewer pores in the carbon framework. Second, with less MgO the crystallinity was improved remarkably, as shown in Figure 1. It proves to be difficult to synchronously develop those two aspects (well-developed pore structure and high crystallinity). Thus, it is necessary to seek a balance between crystallinity and pore structure for diversified applications.

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