Effect of Pyrolysis Temperature on Crystallinity Properties of Acid-Catalyzed Resorcinol Formaldehyde Based Carbon Xerogel

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ABSTRACT

Pyrolysis temperature is a critical factor that influences the structural properties of carbon materials derived from different organic precursors. This study explored the impact of pyrolysis temperature (i.e., 400, 600, and 900 °C) on the crystallinity characteristic of the acid catalyzed resorcinol-formaldehyde based carbon xerogels. The crystallinity properties of the resulting carbons were investigated based on the XRD analysis aiming to understand the transformation of the resulted carbon xerogel microstructure upon thermal treatment. The findings revealed a meaningful correlation between pyrolysis temperature and the crystallinity of the final carbons. Notably, as the pyrolysis temperature increased, the degree of crystallinity of the carbons also increased. Specifically, the carbon xerogel synthesized at 900°C exhibited a turbostratic carbon structure, highlighting the significant influence of high pyrolysis temperature on the graphitization process.

Keywords: Pyrolysis, Resorcinol- formaldehyde gel, sol-gel method, ambient pressure drying.

1. *INTRODUCTION*

Carbon aerogels are intriguing monolithic materials with a wide range of potential applications due to their remarkable properties, including low density, high surface area, high porosity, low electrical resistivity, and controllable structural characteristics. Notably, carbon aerogels synthesized from resorcinol-furfural organic aerogels exhibited a BET surface area ranging from 438 to 900 m²/g, average pore sizes of 17.9 to 22.4 nm, and total pore volumes of 0.20 to 0.27 cm³/g. Among the various materials studied, the resorcinol–formaldehyde system was the most frequently researched, providing a better understanding of reaction parameters [1-3]. The preparation of carbon aerogels typically involves four main steps: sol–gel formation, solvent exchange, drying, and pyrolysis, each significantly impacting the final characteristics of the aerogels. Pyrolysis, the thermal decomposition of organic precursors in an inert atmosphere, plays a pivotal role in determining the final properties of carbon materials. The temperature applied during this process not only facilitates the removal of volatile species but also dictates the degree of carbonization and graphitization. Understanding the relationship between pyrolysis temperature and the resulting crystallinity is essential for optimizing carbon xerogels for specific applications, as their performance is highly dependent on their microstructural features [4-6].

The main objective of the present study was to investigate the effect of pyrolysis temperature on changing in the crystallinity characteristics of the as prepared carbon aerogels as function of pyrolysis temperature. The samples were prepared by pyrolysis of the sol-gel derived Rf aerogels under the ambient drying condition. The pyrolysis condition of the samples also was included temperature variation from 400 to 900 °C.

2. *Experimental*

2.1. Material

Resorcinol (99%), formaldehyde solution (37% wt), as starting materials, Oxalic acid, as acid catalyst were purchased from Merck (Merck Chemical Co) and used without extra purification. Deionized water was

used as solvent for sol preparation and extra pure ethanol (for the purpose of solvent exchange ang aging of the wet gels) *was purchased from Mojallali Company (in Iran) and was used without further purification.*

2.2. Preparation of carbon xerogels

Carbon aerogel samples were synthesized through sol-gel polymerization under a solvent-saturated vapor atmosphere, followed by a pyrolysis step. In a standard procedure, 5 g of resorcinol was dissolved in distilled water and homogenized with 8.1 g of formaldehyde solution. The prepared solution was subsequently mixed with 15 g of a 0.1 molar oxalic acid solution, which served as the acidic catalyst. The mixture was stirred for 5 minutes before being transferred into a polypropylene container. The as-prepared gels were cured in an oven at 60°C to complete the gelation process. For ambient pressure drying, the samples were immersed in ethanol for 12 hours to facilitate solvent exchange. The samples were then subjected to gradual heating and drying: 1 hour at 80°C, followed by 3 hours at 100°C, and finally 0.5 hours at 115°C. The pyrolysis of the as-prepared RF gel was conducted as follows: the samples were cut into appropriate sizes and placed in an electrical ceramic furnace. The temperature was gradually increased from ambient conditions to the target temperatures of 400°C, 600°C, and 900°C under a nitrogen atmosphere.

3. *METHODS OF CHARACTERIZATION*

Investigations about changing in the graphitization level of the synthesized carbon aerogels was proceeded by X-Ray diffraction method (X'Pert MPD, Philips, Holland, using Cu-Ka radiation).

4. *Results and discussion*

The XRD analysis of the prepared carbon xerogels are presented in Fig. 1. According to XRD spectra, in all cases, there are two weak distinct peaks at 2Θ arounds 22 and 43, which are indicative of (002) and (100) planes of graphitic structures, respectively [7-8]. As illustrated in XRD spectra, the as-prepared RF gels exhibited a broad humplike peak indicating the formation of amorphous structure in the synthesized samples. On the contrary, by increase by increase in pyrolysis temperature the broad peaks tend sharpen, implying that the crystalline structure can be developed under the mentioned condition. It can be due to the facilitated the mobile ability of the carbon moieties presented in the RF gels. On the other hand, excessive vibration and movement of carbon components improves crystalline properties and improving the formation process of stacking graphene layers, in turn leading to the building up the (002) interplanar structures.

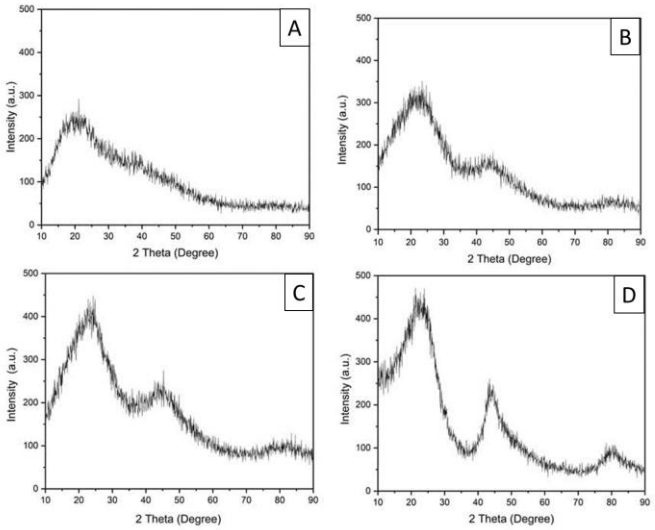

Fig. 1. *XRD analysis from the as-prepared RF aerogel (A), the synthesized carbon xerogels at the different pyrolysis temperatures of 400 (B), 600 (C), and 900 (D).*

Table 1. *presents the graphitic characteristics of the carbon xerogels synthesized as a function of carbonization temperature. The crystalline parameters were determined from the XRD spectra using the JCPDS-ICDD powder diffraction database and PANalytical X'Pert HighScore Plus software (Version 3). The interlayer spacing (d_{002}) and crystalline dimensions (i.e., L_a and L_c) were calculated using Bragg's equation and Scherrer's equation, respectively [9-10].*

$$d_{002} = \lambda\ (2 \sin \Theta_{002})^{-1} \quad (1)$$

$$L_a = 1.84\lambda\ (\beta \cos \Theta_{100})^{-1} \quad (2)$$

$$L_c = 0.94\lambda\ (\beta \cos \Theta_{002})^{-1} \quad (3)$$

Where L_a, L_c, λ, β, and θ represent the crystalline (stacking) width, crystalline (stacking) height, X-ray wavelength, full width at half maximum (FWHM), and peak positions of the 002 and 100 planes, respectively. The layer packing density (ρ) and the number of graphene layers in a stack (N) were calculated using the following formulas [11].

$$\rho = 0.76/d_{002} \quad (4)$$

$$N = L_c/d_{002} + 1 \quad (5)$$

Table 1. *lattice properties of the synthesized carbon aerogel obtained from XRD analysis.*

samples	*2θ (degree)*	*d (nm)*	*L_c (nm)*	*L_a (nm)*	*$\rho\ (g/cm^3)$*	*N (pieces)*
440℃	*22.47*	*3.98*	*0.25*	*0.46*	*0.19*	*1.02*
600℃	*23.35*	*3.72*	*0.23*	*0.34*	*0.19*	*1.03*
900℃	*24.18*	*3.60*	*0.11*	*0.28*	*0.20*	*2.03*

The crystalline parameters reveal that an elevation in pyrolysis temperature results in the formation of carbon structures characterized by a reduced interlayer spacing of the 002 planes. Specifically, the interlayer spacing decreases from 3.98 nm to 0.36 nm as the pyrolysis temperature increases from 400°C to 900°C, indicating a pronounced structural transformation. Notably, higher pyrolysis temperatures also yield crystalline carbons with a smaller lattice diameter. In this regard, the crystalline diameter (L_a) diminishes from 0.46 nm to 0.28 nm as the pyrolysis temperature progresses from 400°C to 900°C. It should be notted that, the significant variations in both the lattice diameter and the d_{002} characteristic can be attributed to the formation of defect-rich graphitic structures. The development of such graphitic structures, accompanied by a reduced stacking thickness of graphene sheets (L_c), confirm the formation of nano-sized graphitic structures at elevated pyrolysis temperatures. Furthermore, the interlayer spacing between graphene layers in the produced carbon xerogels is smaller than the turbostratic characteristic (d_{002} = 3.44), suggesting that the samples are predominantly amorphous carbons with a minimal content of nanographitic structures. This implies that carbonization at varying temperatures (ranging from 400°C to 900°C) leads to the formation of carbon xerogels with a random distribution of graphene sheets. Additionally, the variation in the packing density of graphitic structures confirms that as the pyrolysis temperature increases from 400°C to 600°C, the packing density rises from 0.19 g/cm³ to 0.2 g/cm³, further highlighting the positive influence of temperature on the development of carbons with graphitic structures.

CONCLUSION

This study demonstrates the significance of pyrolysis temperature in controlling the crystallinity properties of carbon xerogels derived from acid-catalyzed resorcinol formaldehyde xerogel. The results provide valuable insights into the thermal transformation of organic xerogels into carbons with tailored microstructural properties, which is crucial for optimizing their performance in various applications. The experimental results revealed that by increase in pyrolysis temperature from 400 to 900 °C all prepared carbon

xerogels are amorphous in nature and the degree of graphitization increased by the increase in the pyrolysis temperature.

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