Time-Efficient Oxalic acid catalyzed Resorcinol–Formaldehyde organic gel

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ABSTRACT

Resorcinol –formaldehyde (RF) aerogels are a class of organic materials that used as precursors of carbon aerogels. Usually, this type of materials prepared via a time-consuming base-catalyzed gelation process from an aqueous sol. In this regard, the acid catalyzed gelation method was proposed, and the physico-chemical properties of the resulted organic gel was investigated. The RF sol was prepared by mixing resorcinol (R) with formaldehyde (F) in catalyst solution (C) in the fixed mol ratios of (1, 2, and 5). The experimental results revealed that the gelation process proceeded in short time of 2 hr and the chemical nature of the resulted acid catalyzed gels was identical to the base-catalyzed RF gels with aggregated type structure of the incremented organic particles.

Keywords: Resorcinol Formaldehyde gel, Sol-gel, ambient drying condition, Aerogel.

1. *INTRODUCTION*

In recent decades, a vast number of research papers have been published on the synthesis of resorcinol-formaldehyde (RF) aerogels, which were initially invented by Pekala in 1989. However, only a few studies focus on acid-catalyzed RF aerogels. Organic aerogels are open-cell foams derived from supercritical fluid (SCF) drying of wet gels. Their large internal void space is responsible for low thermal conductivity, high surface area, and high acoustic impedance [1]. However, the synthesis process of organic aerogels is cost-intensive compared to silica-based aerogels, mainly due to the relatively high cost of resorcinol, time-consuming process, and the high costs of supercritical drying. Investigations to reduce synthesis costs while achieving improved product properties are essential, as these organic RF aerogels serve as precursors for producing carbon aerogels via pyrolysis. Two significant aspects to enhance the manufacturing process include reducing gelation time and avoiding supercritical drying. In base-catalyzed synthesis, reducing the catalyst content leads to a high resorcinol-to-catalyst (R/C) ratio, allowing for ambient drying instead of supercritical drying [2-3]. However, this results in a significant increase in gelation time. Using acids to catalyze the gelation process accelerates the polycondensation reaction of resorcinol-formaldehyde, shortening the gelation time. However, some literature discusses the effects of various acids, such as acetic and hydrochloric acid. Only a few studies focus on the synthesis and characterization of acid-catalyzed RF aerogels [4-5].

The main objective of the present study was to synthesize and characterize time-efficient acid-catalyzed RF gels using oxalic acid as a catalyst under the ambient pressure drying method. The organic gel was synthesized under the fixed mole ratios of precursors. The as-prepared gel was characterized by FTIR, XRD, and FE-SEM analysis, and the obtained results were discussed.

2. *MATERIALS AND METHODS*

Resorcinol (~98%), formaldehyde (35%w) as the reactants, Oxalic acid as the acidic catalyst (C) and ethanol as the solvent exchange agent were obtained from Merck (Merck Chemical CO) and used as received. Double distilled water was used for both sol preparation and aging of the wet gels. The synthesis of the RF aerogels is performed by a sol-gel routine. In this regard, the dissolved resorcinol (5 gr) in distillated water (26.4 gr) was mixed and homogenized with 8.1 gr of formaldehyde solution. The prepared solution was mixed with 1 molar oxalic acid solution (9.1 gr) as the acidic catalyst. Finally, the contents were stirred for 5 min before being poured into a polypropylene container. For the completion of both gelation and aging of the wet gels, the samples were cured in an oven at 40 ºC. For ambient pressure drying, samples were immersed, and the solvent was exchanged in ethanol for 24 h. finally, the samples were heated gradually in an ethanol-rich atmosphere to control the exerted capillary pressure on the RF aerogel. The samples were dried for 2 h at 60 ºC followed by 3 h at 70 ºC and 1 h at 120 ºC.

3. *METHODS OF CHARACTERIZATION*

Chemical bond formation of the organic gel was studied by FTIR spectroscopy under transmittance mode, at a resolution of 4 cm-1 (Bruker Equinox 55LS 101 series, Germany). The microstructure configuration of the samples was observed using FE-SEM (TESCAN, Mira II LMU, Czech Republic) at an acceleration voltage of 15 KV. The graphitization level of the prepared samples was investigated by X-Ray diffraction method (X'Pert MPD, Philips, Holland, using Cu-Ka radiation).

4. RESULTS AND DISCUSSION

The scanning electron microscopy (FE-SEM) analysis from the synthesized RF gel was shown in Fig. 1. According to the obtained morphology investigation, the microstructure of the synthesized gel has a wrinkled spherical morphology with micrometric dimensions ranging from 4-6 µm, resulting from the disordered arrangement of the grown resorcinol-formaldehyde gel layers. The obtained morphology can be attributed to the interaction between the functional groups of oxalic acid and the phenyl groups present in resorcinol. In such condition, in contrast to inorganic catalysts, the presence of oxalic acid functional groups (i.e., -COOH), as a catalyst, lead to the planar arrangement of resorcinol particles adjacent to each other during the condensation polymerization. In this case, the chemical structure of the catalyst has interacted with the resorcinol monomer, resulting in the creation and growth of a nano planar structure as initial seeds in sol-gel process.

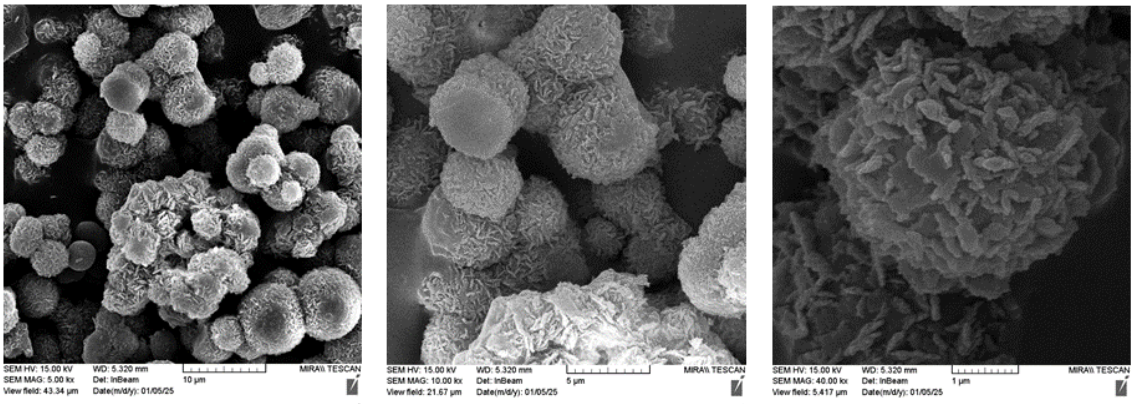

Fig. 1. The FE-SEM analysis from the acidcatalyzed RF gel.

The FTIR spectra of the obtained native RF gel was show in Fig. 1. The observed FTIR absorptions at wave numbers of 2982, 2862 and 1490 cm^{-1} were associated with CH_2 stretching bonds vibration, whereas the broad band at 3480 cm^{-1} is associated with the hydroxyl group presented in the resorcinol ring. The obtained band at 1624 cm^{-1} represents the aromatic stretches, while the bands at 1232 cm^{-1} and at 1080 cm^{-1} were assigned to vibrations of the methylene ether link between phenyl rings in RF structure. The FTIR results

revealed that the chemical bond characteristics of the acid synthesized RF gels was identical to the synthesized RF organic gels in the base condition. On the other hand, synthesis under the acidic condition (using oxalic acid) leads to formation of RF gels with similar characteristic of those prepared under the basic condition [3-7].

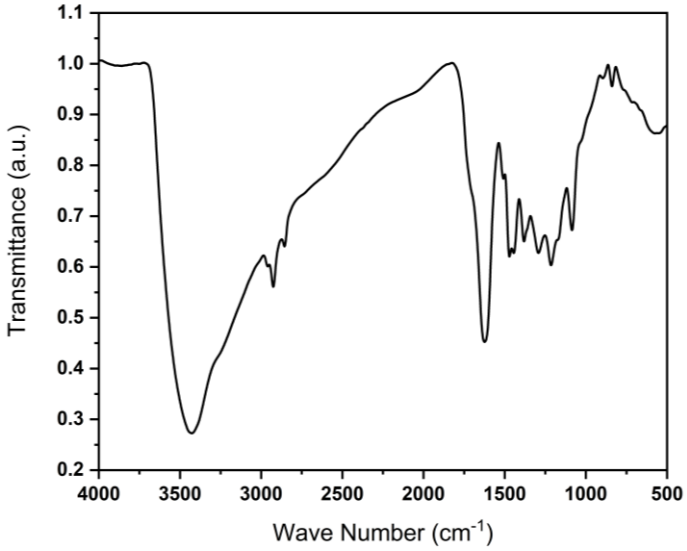

Fig. 2. The FTIR analysis from the acid synthesized RF gel.

The X-ray diffraction (XRD) pattern of the synthesized RF gel under acidic conditions is illustrated in Fig. 3. The resulting diffraction exhibits two broad peaks at 2θ of 21° and a hump like diffraction at 40° related to the 100, 002, and 004 planed of carbon, respectively. This finding indicated that the physical nature of the synthesized gel was amorphous structure. This amorphous nature can be attributed to the disordered arrangement of phenyl rings associated with R during the condensation polymerization process, which leads to a lack of long-range crystalline order in the resulting gel [8-9].

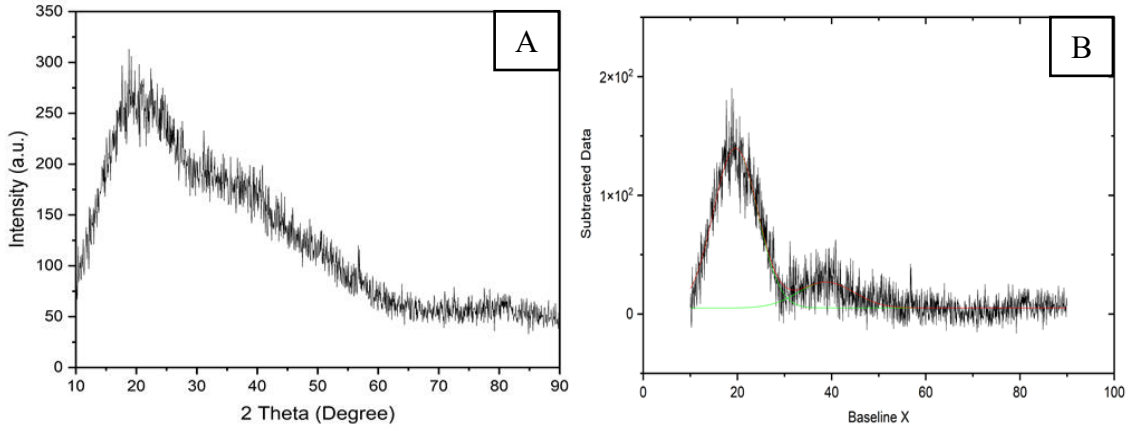

Fig. 3. The XRD pattern obtained from the as prepared RF gel (a). the peak analyzed pattern (b).

5. CONCLUSION

In the present work, the synthesis and characterization of acid catalyzed time-efficient RF gel was synthesized and characterized. The as prepared gel was characterized by FE-SEM, FTIR, and XRD methods.

The experimental investigations show that polycondensation of R with F proceeded in 1 hr under the acidic condition. The results also revealed that the chemical bonding nature of the as-prepared gel was identical with those of prepared gels under the basic conditions. The resulting RF gel comprises an aggregated structure with interconnected organic particles. The crystallinity analysis revealed that the synthesized gel was composed of amorphous structure in nature.

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