Correlation between structure and oxidation behavior of carbon aerogels

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ABSTRACT

In order to investigate the effect of microstructure on oxidation behavior of carbon aerogel, three samples with different pore structure were prepared. These carbon aerogel samples were synthesized via the novel method of sol-gel polymerization in solvent-saturated vapor atmosphere and the following pyrolysis step. The structural characteristics of the unreacted carbon aerogel and the overall rate of oxidation have determined using pore structure analysis methods and thermo-gravimetric analysis (TGA) under non-isothermal condition, respectively. It was found that the initial pore structure and the reaction condition have an important effect on the reaction pathway. The changes in apparent activation energy with the degree of conversion are presumably due to the changes in the oxidation control mechanisms with progress of the reaction and further reveal a multistep kinetic process. So, two different processes were suggested to control the global oxidation kinetics, their relative contribution being temperature and structure-dependent. The reported study may be relevant towards energy storage applications of carbon aerogel at high temperature where the pore structure plays a key role.

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1. Introduction

Carbon aerogels are nanostructure porous carbon materials with high specific surface area. In recent years, much attention has been paid to these materials due to their potential uses in a wide variety of technological applications such as thermal insulation [1,2], catalysis [3], electrochemical double layer capacitors [4,5] and hydrogen and electrical energy storage [6]. Carbon aerogels provide a tunable three-dimensional hierarchical structure by varying the synthesis condition. The tunable structure of carbon aerogels as well as their lower thermal conductivity, compared to the traditional insulating options, makes these materials suitable for insulating of the thermal energy storage systems especially at higher temperature [7,8]. Carbon aerogels are also a good candidate in electrical energy storage systems as the electrical double layer capacitor (EDLC) because they are chemically inert and, unlike the traditional EDLCs, can be made from cheap raw materials. Moreover, the tunable hierarchical structure of carbon aerogels allows one to increase energy density of EDLCs by controlling the pore structure. The storage capacity for electrical energy depends on the presence of micro/mesopores to provide the required surface area, whereas the dynamics of loading and unloading depends on the presence of macropores to facilitate mass transport and provide power density [6].

However, these carbon based materials will react with oxygen at relatively low temperatures (about 400 °C). So, it is necessary to evaluate the thermal performance of carbon aerogels in view of their energy-related applications at high temperature. The reaction of carbon with oxygen has been widely investigated in literature and is generally believed to involve dissociative adsorption of oxygen on the active sites to form surface-oxygen complexes and the subsequent desorption of the surface oxides to gaseous products [9–13]. In the case of porous carbons, the oxidation reaction occurs in a diffusion zone rather than a sharp boundary, therefore, the diffusion of oxygen molecules within the porous structure prior to adsorption adds another important step in the reaction mechanism [14]. So, the oxidation of porous carbon can be considered as a multiple step reaction with diffusion, adsorption, chemical reaction and desorption in series. Many parameters related to porous carbon structure such as surface area [15,16], pore diffusivity and pore structure [17] are thus expected to involve in determination of the overall reaction rate.

It has been confirmed that thermally motivated reactions in the solid state usually involve multiple steps that contribute to the overall rate of reaction measured from thermo-analytical methods [18]. Isoconversional methods have been used broadly for describing the kinetics of solid state reactions because it presents a fortunate compromise between the single-step Arrhenius kinetic

treatments and the prevalent occurrence of processes whose kinetics are multi-step and/or non-Arrhenius. However, the mechanisms of the solid state processes are too complicate to be characterized only by these methods. The application of these methods only helps one to distinguish the multi-step nature of the reaction and the complexities in reaction kinetics [19,20]. The objective of this paper is to study the relative significance of the microstructural parameters on the oxidation behavior of carbon aerogel. For this purpose, three samples with different pore structure are synthesized using the novel method of sol-gel polymerization in solvent-saturated vapor atmosphere (by changing only the initial sol concentration of the precursor). The effect of pore structure on the overall rate of oxidation was then investigated during the temperature-programmed oxidation analysis and by studying the structure of unreacted carbon aerogels. The nonisothermal TGA data were also treated by model-free isoconversional methods for evaluating the variation of the apparent activation energy with degree of conversion. Also an attempt was made to explore the porous carbon oxidation mechanism by comparing the thermal oxidation behavior of three carbon aerogel samples at different level of reaction conversions and at different heating rates.

2. Experimental

2.1. Material

Novolac resin (IP 502) manufactured by Resitan Company (in Iran) was chosen as the precursor for preparation of organic aerogels. The novolac resin contained 9 wt% hexamethylenetetramine (HMTA) as the curing agent. 2-Propanol alcohol was purchased from Mojallali Company (in Iran) and was used without further purification.

2.2. Preparation of carbon aerogels

Carbon aerogel samples were synthesized via the novel method of sol-gel polymerization in solvent-saturated vapor atmosphere (developed in our laboratory)[21] and the following pyrolysis step. The initial sol concentration in the sol- gel polymerization was the only factor varied for preparing the carbon aerogel samples with different microstructure. First, three solutions with resin concentration of 20, 30 and 40 wt.% were prepared in 2-propanol solvent. Then, these solutions were cast in PTFE molds and placed into an autoclave containing small amount of pure solvent. After sealing, the autoclave temperature was raised to 443 K and held at this temperature for 5 h. The organic gels thus obtained through the sol-gel polymerization under the saturated vapor pressure of solvent at 443 K (and pressure of about 1.5 Mpa), were subsequently dried according to the thermal cycle of 298 K for 24 h, 363 K for 24 h, 393 K for 24 h and 413 K for 4 h. Finally, the resultant organic aerogels were carbonized in a furnace under a constant flow (0.2 lit/min) of nitrogen to prepare carbon aerogel samples. The carbonization process was performed at the heating rate of 10 °C/min with 15, 30 and 180-min pauses at temperatures of 523, 823 and 1073 K, respectively. The carbonized sample obtained from primary resin concentration in sol of 20, 30 and 40 wt% are marked as CA20, CA30 and CA40, respectively. Actually, in this work, the key parameter for controlling the pore structure of carbon aerogels is the primary mass concentration of novolac in sol solution.

2.3. Characterizations

Apparent density (ρ_a) of the carbon aerogels were calculated by measuring the weight and physical dimensions of the samples. The solid network bulk density (skeletal density, ρ_s) was determined by helium pycnometry (AccuPyc 1330, Micromeritics, USA). Porosity (ε) of the samples were calculated from apparent and skeletal density values ($\varepsilon = 1 - \rho_a/\rho_s$).

The structural properties of carbon aerogels have been investigated by Field Emission Scanning Electron Microscopy (FESEM), nitrogen adsorption-desorption and X-ray diffraction methods. Diffraction patterns of the samples were recorded using Philips XPert MPD diffractometer (made in USA) with CoKα (λ=0.179 nm) radiation source in a range of diffraction angle 2θ from 5° to 70°. Sorption isotherms of nitrogen were determined at 77 K using a Belsorp-mini II volumetric adsorption measurement instrument (made in USA). Specific surface areas and total micro-meso pore volumes (V_{tot}) are determined by the standard BET (Brunauer- Emmett-Teller) analysis. The macropores volume was estimated according to the relation $V_{mac} = \left(\frac{\varepsilon}{\rho_a}\right) - V_{tot}$. Mercury porosimetry was also performed from 0.01 to 200 MPa (PASCAL 440 Thermo Finnigan, Italy) in order to obtain the required information for calculating the tortuosity factor of the carbon aerogel samples.

Thermal oxidation of carbon aerogel samples were studied by thermo-gravimetric analysis (TGA) under non-isothermal condition. The measurements were performed on a TGA 1 Star System analyzer (Co. Mettler Toledo, Switzerland). After placing about 8 mg of the samples in aluminum pans, the temperature was raised at a constant heating rate under the constant air flow of 50 ml/min. For evaluating the variation of the apparent activation energy with progress of the oxidation, experiments were performed at three different heating rates (3, 6, 10 °C min^{-1}).

3. Results

3.1. Structural analysis

Sorption isotherms for carbon aerogel samples were shown in Fig. 1. The structural characteristics determined from these isotherms, using standard analysis methods, as well as the physical properties of carbon aerogels were reported in Table 1. As seen from Table 1, the apparent density and pore structure of carbon aerogel samples are mainly controlled by the resin concentrations in initial sol. Increasing the resin concentration results in a more dense aerogel with lower porosity value. This further leads to a decrease in the macropores and an increase in the mesopores volume as considered from Table 1. The CA30 sample has the maximum BET surface area while the maximum amount of total micro-meso pore volume belongs to CA40 sample with the highest solid content. About 89% of the entire pore volume of the CA20 sample was contributed by macropores while this value was just 11% for the CA40 sample. Mesopores with contribution of 73% of the entire pore volume are dominant in the structure of the CA40 sample. So, the CA40 and CA20 samples are considered as a meso and macro porous material, respectively.

The plot of pore volume density ($\Delta V/\Delta r$) against pore size (r) derived from adsorption branch of nitrogen isotherms using BJH analysis are shown in Fig. 2. This type of presentation of the pore size distribution is identical to that recommended by IUPAC [22]. By normalization of the pore volume with respect to the pore size in this method, the data are comparable within the whole range of pore radius. The area under the curve in a pore radius range yields the pore volume in that range. As it is evident from Fig. 2 the samples CA30 and CA40 show a great variation in pore size within the range of 2–50 nanometers while the structure of CA20 sample is mainly formed by the micropres with the size less than 2 nanometers. Moreover, the sample CA40 with the highest area under the pore volume density curve shows the maximum total