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Catalytic graphitization behavior of phenolic resins by addition of *in situ* formed nano-Fe particles

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ABSTRACT

This work presents the catalytic graphitization process of phenolic resins (PR's) by addition of *in situ* nano-Fe particles as catalyst. Pyrolysis treatments of prepared compositions including various contents of nano-Fe particles were carried out at 600–1200 °C for 3 h under reducing atmosphere and graphitization process were evaluated by different techniques such as X-Ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), High Resolution Transmission Electron Microscopy (HRTEM), Simultaneous Thermal Analysis (STA) and Raman spectroscopy that mainly performed to identify the phase and microstructural analysis, oxidation resistance and extend of graphitized carbon formation. Results indicate that, *in situ* graphitic carbon development were already observed after firing the samples at 800 °C for 3 h under reducing atmosphere, increasing temperature and amount of nano-Fe led to a more effective graphitization level. In addition, the different nano crystalline carbon shapes such as onion and bamboo like and carbon nanotubes (CNTs) were *in situ* identified during graphitization process of nano-Fe containing samples. It was suggested that formation of these different nano carbon structures related to nano-Fe catalyst behavior and the carbon shell growth.

1. Introduction

It is well known that thermosetting phenolic resins (PR's) is an important carbonaceous binder of Oxide-C refractories because of many good properties such as high fixed carbon rate, good wettability with oxide and graphite, high green strength and low hazardous environmental issues [1–4]. Compare to above good potential, PR's are classified as non-graphitizing carbon binders and isotropic glassy carbon derived from these materials would not be spontaneously graphitized, even when Oxide-C refractories heated to high temperatures. In addition, residual glassy carbon has poor oxidation resistance, low thermal stability and high brittleness that will negatively affect some of the main refractory properties such as chemical corrosion, thermo-mechanical strength and thermal shock resistance [5–9]. Therefore, some efforts have been performed on PR's modification by adding various metallic antioxidants in nano/micro sizes and, nano carbon sources such as carbon nano tubes (CNTs), carbon nano fibers (CNFs) and carbon black (CB) [10–14]. However, these modification methods still need to be further optimized. Recently, different researches have been reported to induce the crystallization of non-graphitic PR's binders so-called catalytic graphitization that during pyrolysis of phenolic resin, glassy isotropic carbon convert into graphitic carbon by addition of some catalytic agents. Transition metallic elements (Ni, Co, Cu, and Fe), various compounds including organometallics, soluble metal salt and metal oxides based on transitions metals are the main ingredients that can be used as catalytic agents. Furthermore, it is well suggested that in order to higher graphitization level, these additives must be well dispersed in the resin inside structure as micro or nano-powder, suspension or even dissolved in a solvent and available as individualized molecules in the beginning of the resin carbonization process between 400 and 500 °C [15–19].

On the basis of Oya et al. [20] studies, interaction of the catalytic agents with glassy carbon during carbonization process accomplish based on two routs "Generation-Decomposition" and "Dissolution-precipitation" as main mechanisms. In the first mechanism, graphitic carbon was precipitated at high temperature from carbide compound that formed by reaction of carbon and metallic particles. However, in later mechanism the non-graphitic carbon is continuously dissolved into the metal structure and precipitated as graphite after over saturation. When phenolic resins heat treated, some reducer gaseous consist of H_2, C and CO are produced during pyrolysis process. These

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