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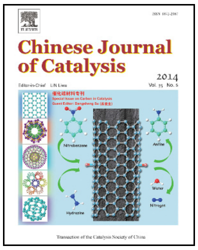

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Low-temperature graphitization of amorphous carbon nanospheres

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ABSTRACT

The investigation by SEM/TEM, porosity, and X-ray diffraction measurements of the graphitization process starting from amorphous carbon nanospheres, prepared by glucose carbonization, is reported. Aspects studied are the annealing temperature in the 750–1000 °C range, the type of inert carrier gas, and time of treatment in the 2–6 h range. It is investigated how these parameters influence the structural and morphological characteristics of the carbon materials obtained as well as their nanostructure. It is shown that it is possible to maintain after graphitization the round-shaped macro morphology, a high surface area and porosity, and especially a large structural disorder in the graphitic layers stacking, with the presence of rather small ordered domains. These are characteristics interesting for various catalytic applications. The key in obtaining these characteristics is the thermal treatment in a flow of N_2. It was demonstrated that the use of He rather than N_2 does not allow obtaining the same results. The effect is attributed to the presence of traces of oxygen, enough to create the presence of oxygen functional groups on the surface temperatures higher than 750 °C, when graphitization occurs. These oxygen functional groups favor the graphitization process.

1. Introduction

Nanocarbons (also indicated as nano-structured carbons) indicate carbon materials having a tailored nanoscale dimension and functional properties critically depending on their nano-scale features and architecture [1–13]. The role of the nanostructure in determining the performance and catalytic behavior of carbon materials is well known [1,14,15], and thus these materials open interesting opportunities for catalysis.

Nanocarbons include many different types of carbon materials such as nano-fibers, -coils, -diamond, -horns, -onion, fullerene, etc. They find increasing interests as catalysts and may be actually considered as a novel class of catalytic materials. The range of applications goes from electrocatalysis (being a conductive support) and photocatalysis to novel supports for metal particles (for applications going from environmental protection to catalytic syntheses). In addition, their use as metal-free catalysts or electrocatalysts (related to the specific type of active sites present on the surface of the nanocarbon, as consequence of defects, doping and surface treatments) was

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shown to offer new exciting possibilities [16–21].

Their catalytic properties derive from their unique combination of chemical properties, inferred by sp, sp^2, and sp^3 hybridized bonds, with the several structural arrangements, i.e. linear, planar, or tetrahedrical geometries [22]. Metal-free nanocarbons show interesting catalytic properties in various reactions, going from alkane activation and oxidative dehydrogenation [23–25] to the selective gas-phase oxidation of acrolein to acrylic acid [26].

In the latter reaction, for example, the sp^2 carbon acts as a bifunctional catalyst: the nucleophilic oxygen atoms terminating the graphite (0001) surface abstract the formyl hydrogen and the activated aldehyde gets oxidized by epoxide-type mobile oxygens. In general, for sp^2 nanocarbons, high-energy sites provided by the dangling bond of the sp^2 hybridization are located at the edges (prismatic sites). These sites are saturated by heteroatoms (depending on the pre-treatment), providing a rich surface catalytic reactivity for both acid-base and redox chemistry. If the graphitic sheets contain defects in form of pentagonal, heptagonal, or larger non-hexagonal units, an additional charge present can assist the activation or dissociation of adsorbing molecules. In addition, if the graphitic sheets are curled, then the strain on the sp^2 centers leads to charge localization and increases the poor reactivity of the basal plane.

The nanostructure, type of surface species, and hybridization of surface carbon atoms, which may be enhanced from the presence of strains and curvatures as well as degree of graphitization, are all aspects determining the catalytic performance. An example is the synthesis of phosgene, which is still produced using carbon as industrial catalyst in an annual amount of about 5–6 million tons, in spite of the well-known safety issues (high toxicity of the products and hazardous reaction conditions) [27]. Phosgene is a chemical intermediate used in the manufacture of important industrial products such as polyurethanes, polycarbonates, pharmaceuticals, and agrochemicals. Metal-free carbon catalysts show better performance than other materials, but the specific nature of the carbon strongly influences the performance [28], although the exact nature of the active sites is still unknown. In fact, Cl_2 dissociation and further CO halogenation are probably the first steps in the reaction of phosgene synthesis from CO and Cl_2, and it is known that reaction mechanism considerably depends on the nanocarbon stucture [29].

In addition to specific nanostructure properties, the carbon-based catalysts should possess porosity characteristics different from those necessary in other relevant areas of application of carbon materials (i.e. sorption, molecular separations, and gas storage), because microporosity may reduce catalyst effectiveness. Mass transport, particularly in fast reactions, can significantly limit the reaction rate, but equally relevant, in strongly exothermic reactions, is heat transport, which may result detrimental not only in catalytic performance (especially selectivity), but also in long-term stability of the carbon catalyst. The degree of graphitization is a way to improve heat transfer and control surface reactivity. For this reason, the specific nanostructure and surface nature of carbon catalysts play a specific role in their performance for phosgene synthesis [28].

Carbon nanospheres are a novel type of nanocarbon materials, which attracted interest for the presence of different hybridized bond surface sites and of curling planes, which may change the reactivity of graphitic sheets. Several papers have been published on these materials, for applications going from manufacture of electrodes to catalysis [30–38], showing how the graphitization degree of the carbon plays an important role in determining its properties. Nevertheless, a key issue is to avoid the destruction of the other important characteristics for reactivity, such as porosity and type of surface species (related to hybridized bond surface sites, defects, etc.).

Usually, the graphitization process is made by applying high current densities or temperatures (> 2500 °C) [39–41]. Apart the need to use a proper graphitizable carbon precursor such as CNF [42,43], the main disadvantages of these processes are the high energy consumption, the low yield, and the surface area loss. There is also a change in the characteristic nanostructure. Briston et al. [44], for example, have analyzed the transformation of amorphous porous carbon nanospheres under Joule heating, observing significant carbon ordering resulting in the formation of a 3D network of buckled graphitic sheets. The peculiar carbon reactivity characteristics are thus lost in the process.

Hence, some attempts have been made in order to graphitize carbon at relatively low temperature (<1000 °C) by means of metals (Fe, Co, Ni, etc.), which accelerate the initiation [45,46]. Despite the wide application of these methodologies, the encapsulation of such metals into the framework leads to the need of further purification steps.

Therefore, in this work we discuss a method to graphitize amorphous carbon nanospheres, obtained by hydrothermal decomposition of glucose, without using metals and with a procedure allowing to maintain high the surface area minimizing changes in the surface nanostructure. The goal is to obtain a crystalline arrangement with onion-like structure, without surface area loss. We investigated here the role of the main experimental parameters in the treatment (annealing temperature at 750 or 1000 °C, type of inert carrier gas, time of stream in the 2–6 h range) and how they influence the morphological characteristics of the carbon materials obtained as well as their nanostructure.

2. Experimental

2.1. *Amorphous carbon synthesis*

Pure glucose (10 wt%) was dissolved in 180 mL of distilled water to form a clear solution and placed in a Teflon-sealed autoclave at 200 °C for 20 h. The product was then separated by filtration and washed several times with hot water, acetone, and ethanol solvents. Then it was dried at 100 °C and further treated at 200 °C for 2 h. The quantitative yield was about 20 wt%. This sample is indicated as CHT.

2.2. *Graphitization procedure*

For each graphitization procedure, ca. 200 mg of CHT were