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Carbon microspheres preparation, graphitization and surface functionalization for glycerol etherification

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ABSTRACT

An easy and cost-effective method to prepare mono-disperse carbon microspheres *via* a hydrothermal carbonization process (CHT) under moderate conditions (200 °C) has been investigated. The preparation was carried out using glucose in aqueous solution. The results clearly revealed that the procedure employed allowed obtaining amorphous microspheres, 200–300 nm in size, and spheres of 1–2 μm, characterized by a surface area close to 600 m²/g. TEM-EELS and XRD analyses demonstrated that the crystallinity grade of carbon micro-spheres significantly increases after N₂ treatment at 1000 °C for 6 h. Moreover, the presence of surface functional groups, revealed by DRIFT analysis, allowed functionalizing the carbon spheres by sample inorganic acid treatment or by inorganic acid treatment followed by impregnation with fluorinated superacid ionomer (Hyflon). These catalytic systems resulted to be very active in glycerol etherification reaction, allowing obtaining, differently from a commercial A15 catalyst, a mixture of *tert*-butylethers containing a very low amount of side products.

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1. Introduction

The preparation of spherical carbon materials has recently received particular attention because of their potential use as lubricant, polymer additives, precursor for synthesis of diamond films [1], as anode material for Li batteries [2,3], adsorbent and supercapacitor [4–6]. Carbon microspheres (CMS) can be prepared by different methods [7–11] although the hydrothermal synthesis results to be the most simple way to obtain carbon spheres characterized by regular spherical form and very probably it can also represent the most suitable route for the scale-up of synthesis process [12,13]. Different materials can be used for the preparation of CMS by thermal treatment, such as xylose and fructose [14], glucose [15], glucose solution loaded into a microwave reactor [16], polyethylene (plastic waste) [17,18] *etc.* CMS obtained with such procedures are generally characterized by a diameter ranging from 200 to 500 nm and in all cases the prevailing carbon structure is amorphous. This could be a limitation if a high graphitization grade is required for specific application. Recently, a review regarding the

graphitization by a thermal treatment of carbon nanofibers (CNFs) has been published [19] and describes the mechanisms of transformation of CNFs into graphite despite high temperature are required (2800 °C). In this study, the graphitization of amorphous microspheres, prepared by hydrothermal treatment of glucose (CHT) and then heat treatment under controlled environment at 1000 °C, has been investigated. Moreover, carbon microspheres were used as carrier to prepare a superacid catalyst using inorganic acids like sulphuric acid or inorganic acid as nitric acid and then Hyflon (organic ionomer) as active specie. The catalytic behaviour of such novel systems has been investigated in glycerol etherification, a reaction which is strongly influenced in terms of product selectivity and side products formation by the surface properties of the carrier used [20].

2. Experimental section

2.1. Preparation of carbon spheres by hydrothermal treatment of glucose (CHT)

Pure glucose (18 gr–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

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and washed several times with hot water, acetone and ethanol to remove impurities. Then carbon powder was dried at 100 °C and further treated at 200 °C for 2 h in air. The obtained sample was labelled as CHT.

2.2. Thermal treatment of CHT

The carbon micro-spheres produced by hydrothermal method were treated by putting 200 mg of sample in a vertical fixed bed reactor inserted in a well isolated electric oven and in each experiment a single parameter was changed: (i) annealing temperature (750 or 1000 °C), (ii) time on stream (2 or 6 h), (iii) He or N₂ fed at 100 STP mL/min.

2.3. Functionalization of CHT

Carbon microspheres have been functionalized with inorganic acids by exploiting two different methodologies, here reported.

CHT-S. Concentrated H₂SO₄ has been added to a given amount of CHTs, by maintaining a low flux of N₂ and the magnetic stirring for 10 h. Then the mixture has been slowly washed with hot deionized water until the pH 5.5 was reached. The solution was filtered with isopore membrane filters and then the recovered powder sample was maintained in oven at 110 °C for 12 h.

2.4. CHT-NHy

A determinate amount of CHT was immersed in concentrated HNO₃ at room temperature. After washing with a flux of N₂, the system was maintained at 80 °C for 2 h with a magnetic stirring and then cooled to room temperature in N₂ flux. At this point the sample was neutralized with sodium hydroxide and washed several times, filtered and dried at 110 °C (CHT-N). The CHT-N was impregnated by incipient wetness procedure using an alcoholic solution containing 5% of fluorinated ionomer (Hyflon-730) furnished by Solvay-Solexis. Then the catalyst CHT-NHy was dried at 100 °C for 2 h.

2.5. Chemical-physical characterization

The thermogravimetric differential scanning calorimetry (TGA-DSC) analysis was performed by using a thermo-balance Netzsch STA 409 instrument. The analyses were carried out with a heating rate of 10 °C min⁻¹ from 20 to 920 °C in static air atmosphere.

X-ray powder diffraction (XRD) measurements were carried out using a Philips X-Pert diffractometer with a monochromatic Cu K α ($\lambda = 1.54056 \text{ \AA}$) radiation at 40 kV and 30 mA. Data were collected over a 2 θ range of 10°–100°, with a step size of 0.04° at a time per step of 3 s.

The morphology of the samples was investigated by scanning electron microscopy (SEM-EDX) using a Philips XL-30-FEG SEM at an accelerating voltage of 5 kV. To ensure the high quality of images, the samples were previously treated with Au using a gold sputter coater device. For elemental analysis, the energy dispersive X-ray (EDX) analyzer was employed by using un-pretreated samples.

Carbon structure was investigated by transmission electron microscopy (TEM) using both a Philips CM12 microscope (resolution 0.2 nm), provided with a high resolution camera, at an accelerating voltage of 120 kV and a 300 kV Titan 60-300 (FEI, Netherlands) transmission electron microscope equipped with imaging Cs-corrector, gun monochromator and Quantum GIF (Gatan, USA) EELS spectrometer. Specimens for TEM analyses were prepared by ultrasonic dispersion in *i*-propyl alcohol adding a drop of the resulting suspension onto a holey carbon supported grid.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were obtained in air, at 4 cm⁻¹ resolution, on a Nicolet 380 Thermo

Fisher spectrophotometer, equipped with a DTGS detector. Samples were diluted ($\approx 5 \text{ wt.}\%$) in KBr powder.

The measures of the acid capacity of catalytic systems were performed by potentiometric titration. Prior to each measurement, about 200 mg of catalyst were placed under agitation for 17 h in 3.5 M NaCl. After ion exchange, the solutions were filtered through ashless filter papers (Whatman) and poured into a closed 250 mL beaker with inlets for addition of the basic solution and a pH electrode (Metrohm probe 6-1103.000 Pt100/B/2). The electrode for pH measurement was calibrated with two buffer solutions and the system was thermostated and maintained under agitation. The solutions were titrated with a 0.01 N NaOH, added dropwise by an automatic dispenser with an accuracy of $\pm 0.01 \text{ mL}$ (Metrohm 751 GPD Tritrino). The stabilization of the pH was automatically monitored by an acquisition device and data processing.

2.6. Catalytic activity in etherification reaction of glycerol

The etherification reaction of glycerol has been carried out in liquid phase in a 90 cm³ stainless steel reactor under a stirring frequency of 1200 min⁻¹. Experiments were performed by operating at an isobutene/glycerol molar ratio of 4 (RIB/Gly), at 70 °C, under autogeneous pressure (2–11 bar) and by using a catalyst amount of 7.5 wt.% with respect to glycerol weight ($R_{\text{cat/Gly}}$). A well defined amount of glycerol and the catalyst were loaded into the reactor; before the addition of IB, the reaction environment was flushed with nitrogen to remove the air. Then a given amount of liquid isobutylene, previously fed into a graduated tank, was injected into the reactor under 5 bar of nitrogen pressure. At the end of the run, the reactor was cooled down in an ice-bath, thus allowing condensation of the gas phase compounds. The liquid reaction mixture was analysed off-line by a gas chromatograph, HP 6890N, provided with a capillary column HP Innowax (1, 30 m; i.d., 0.53 mm; film thickness, 1.0 μm). Amberlyst[®] 15 dry (A-15) was used as a reference catalyst. Anhydrous glycerol (purity $\geq 99.5\%$), supplied by Fluka (Buchs, Switzerland), and isobutylene 3.0, by GHC Gerling HOLZ% Co. Handels GmbH (Hamburg, Germany), were used as reactants.

3. Results and discussion

3.1. Graphitization process of CHT

In Table 1 the surface areas (S.A.), pore volumes (P.V.) and average pore diameter (A.P.D.) values of fresh and treated CHT samples are reported. CHT sample has a very high surface area, close to 840 m²/g_{cat} with a high contribution of the micropore fraction (503 m²/g which corresponds to 60% of the total area). The N₂ treatment at 1000 °C for 2 h causes a surface area decreasing to 603 m²/g_{cat} (about 28%) with an increasing of micropore percentage, or rather 400 m²/g which corresponds to 66%. A longer thermal treatment allows recovering the surface area extent (770 m²/g_{cat}) with a further increasing in the microporosity percentage (553 m²/g_{cat}, 71%). This is consistent with the reorganization of the structure due to graphitization, which occurs together with the loss of low stable species present in the amorphous carbon (as typically occurs in preparing activated carbons). The treatment under inert He flow, instead of N₂, at 1000 °C for 6 h, does not lead to a S.A. change of CHT sample.

The adsorption/desorption isotherms obtained at -196 °C of CHT sample are reported in Supplementary data (Fig. S1). No hysteresis, typically observed in case of mesoporous structure [21], was observed; this could be due to a very narrow window of porosity distribution of sample which is so close to the upper-limit of microporous structure (2 nm). By considering the importance of thermal stability of carbon in presence of oxygen, thermo-gravimetric anal-

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