SUPERACID MESOPOROUS CARBONS BASED ON SULFATED Zr

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Abstract

In this brief communication we report the successful preparation of a promising material with acidic properties from starch-derived mesoporous carbon (SMC), functionalized with sulfated zirconia. The process of assembling P123, starch, zirconia and silicon produces ordered mesoporous carbon modified with Zr. Reaction time and temperature are essential to avoid the appearance of poorly assembled or unsightly structures, reducing the surface area and the size of the pores. Zr-SMC has a surface area of approximately 1300 m^2 g^{-1}, and the total pore volume of 0.94 cm^3 g^{-1}, composed mainly of mesopores with an average pore size of 3.5 nm. The composition of the surface and the chemical states of the elements did not reveal ZrO_2 as isolated clusters. Through the thermodesorption of the pre-adsorbed ammonia in the sulfated Zr-SMC, the total ammonia retained is 1.80 mmol / g at high temperature, exhibiting medium to strong acidity.

1. Introduction

Starch Mesoporous carbon (SMC) has attracted attention as a new material due to its applications as drug carriers, catalyst support and energy storage medium [1]. Starch is a nontoxic and renewable carbon precursor and a natural polysaccharide compound; it is abundant and contains more than 49% of oxygen. High content of oxygen in starch results in the surface of starch-derived porous carbon with many hydrophilic groups, which can be widely functionalized in different applications. The carbohydrates available in biomasses are promising resources because they are the main source of natural carbon, renewable and relatively economical [2]. Recently, heterogeneous acid catalysts such as sulfated zirconia [3] and tungsten zirconia [4] have been informed. This research reports on our ongoing efforts to advance in the design of an acid catalyst based on carbon nanostructure. Thus, we developed a SMC-based acid catalyst functionalized with sulfated zirconia with the typical carbon structure of graphite. The functionalization with sulfated Zr groups leads the catalyst to exhibit super-acid properties.

Methods

The synthesis of materials was conducted according to the literature [5]: starch (4.0 g), copolymer triblock, poly (ethyleneglycol) -poly (propyleneglycol) -poly (ethyleneglycol) (Pluronic P123, Sigma-Aldrich) 8.0 g and 320 mL HCl solution (2 M) were mixed in a Polypropylene bottle. The mixture was maintained at 35 °C in a water bath for 6 h under

constant stirring. Then, 18.4 mL of tetraethyl orthosilicate (TEOS, 98%, Sigma- Aldrich) and Zirconium (IV) oxide chloride (99.99%, Aldrich) reaching to a solution with Si/Zr= 20 molar ratio. After stirring for 24 h, the solution was placed in an oven for 24 h at 100 °C without further stirring. The material previously washed was dried at 35 °C in a vacuum oven. The obtained precipitate (1 g) was then treated with 10 mL deionized water and 98 wt. % H_2SO_4 (1 mL) under stirring for 12 h, and pre-carbonized at 100 °C for 6 h. The pre-carbonized sample was calcined at 850 °C under nitrogen flow for 2 h. The resultant carbon/silica composite was washed with 40 wt. % HF solution to extract silica from the carbon framework. Finally, the material was washed with deionized water and successively dried, obtaining SMC material. Mesoporous carbon was functionalized with H_2SO_4 to become sulfated. The new prepared material was called Zr-SMCs, containing an atomic S/Zr ratio around 0.94(±0.1) and total sulfated zirconia approximately 1.35 mmol/g of the catalysts, calculated on the basis of induced coupled plasma emission analysis (ICP).

The samples were characterized by BET (Brunauer–Emmett–Teller, X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) X-ray Photoelectron Microscopy (XPS) and programmed thermodesorption of ammonia (NH3 TPD). XRD results were acquired using a PANALITYCAL Phillips X'pert XDS diffractometer with a diffractometer beam monochromator and a CuKα radiation source. The BET surface area and pore size distribution of the material were analyzed by nitrogen adsorption using a surface area analyzer (Quantachrome / Autosorb1). Chemical states of the elements of sulfated-Zr-SMC were identify by XPS, acquired on a Microtech Multilb 3000 spectrometer, equipped with a hemispherical electron analyzer and MgKα (hv=1253.6 eV) photon source. The surface morphology of the SMC was characterized by the scanning electron microscopy performed in a JEOL JSM-6610LV and the acid properties by the ammonia-TPD, in a Micromeritics Chemisorb 2720 equipment. The samples were pretreated with N_2 at 400 ° C for 3 h. Subsequently, at room temperature, it was put in contact with NH3 vapors for 45 min. NH_3-TPD profiles were collected under He flow at 20 mL / min and a heating rate of 10 ° C / min. from room temperature to 700 ° C. During the preparation process, P123, starch, and silicon and zirconium can self-assemble, at temperatures and times of approximately 100°C and 24 h [5]. The reaction time is critical (less than or greater than 24 h) and higher temperatures appear poorly assembled or dreadful in the structure, reducing the surface area and the size of the pores.

Results and Discussion

Figure 1 shows the diffraction patterns of the SMC: at low-angle and inset at high-angle. At low- angles, two signals indexed as reflections (1 0 0) and (1 1 0), respectively, are observed. Both signals can be associated with hexagonal symmetry of p6mm.
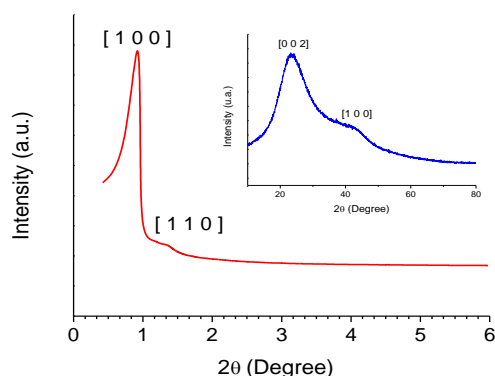

Figure. 1. Low-angle X-ray diffraction and inset at high-angle of SMC

The inset Figure 1 shows two broad signals at high angles, which can be indexed to the (002) and (100) planes typical of graphite carbons. The material has many uniform macropores on its surface characteristics of mesoporous carbon (Figure 2a). Figure 2b shows typical hysteresis loops with capillary condensation (P/Po > 0.55) of Zr-SMCs. The hysteresis loops correspond to isotherm type-IV, indicating a mesoporous structure.

The hysteresis loops of SMCs show H3 characteristics, which can be attributed to slit-shaped pores. Zr-SMC has a large surface area of up to 1300 m^2 g^{-1}, and a total pore volume of 0.94 cm^3 g^{-1} (Figure 2b) composed mainly of mesopores with an average pore size of approximately 3.5 nm (Figure 2c). ZrO_2 crystals were not detected, indicating that sulfated zirconia interacts with the walls of SMC, with the absence of clusters of metallic oxides dispersed on its surface, such as we corroborate with XRD and XPS studies (Figure 3).
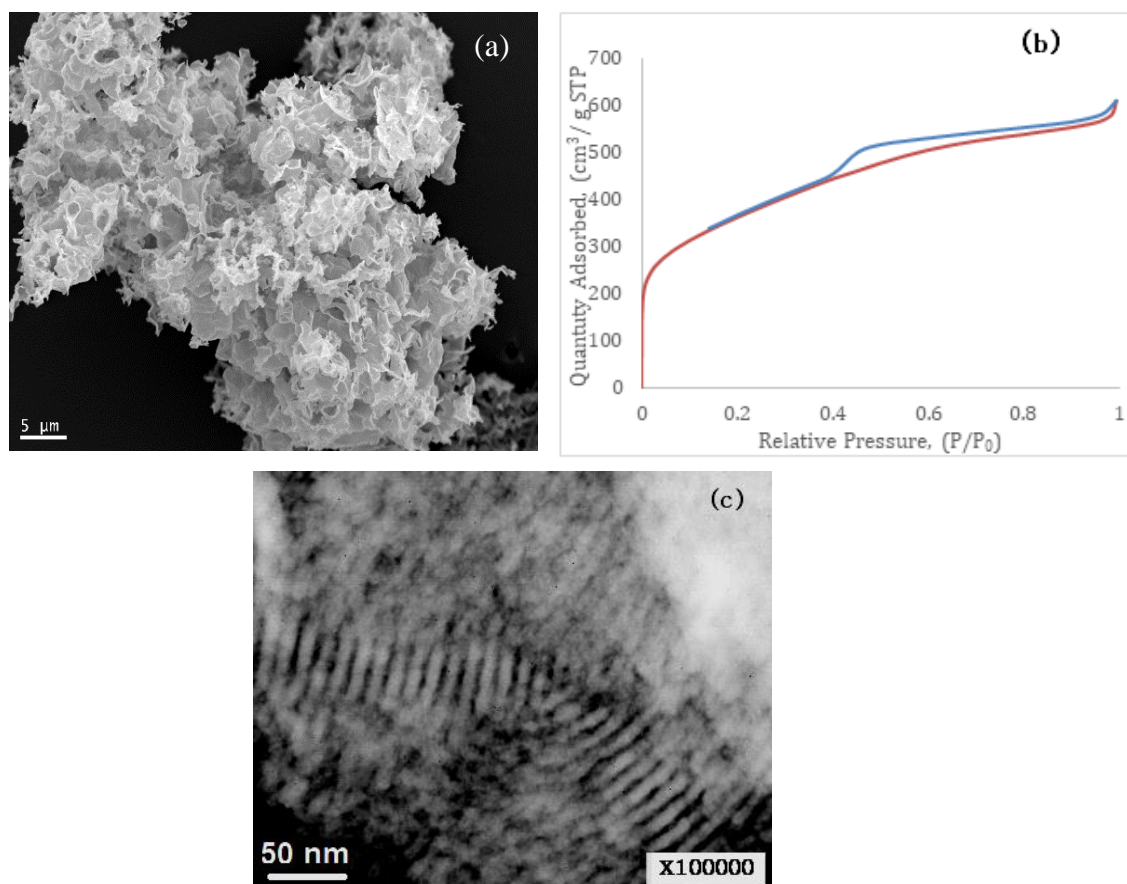

Figure 2. SEM image (a), BET Isotherm (b) and TEM image (c) of SZr-SMCs

The surface composition and chemical states of the elements of sulfated-Zr-SMC were studied using XPS (Fig. 3). The species S-O or S=O that are attributed to S2p appear as broad signal around 170 eV. In addition, Zr signals ($3d_{5/2}$ and $3d_{3/2}$) located around 182.5 eV and 185.0 eV (±0.2) do not correspond to pure ZrO_2 [6]. It can be deduced that the interaction of $SO_4^=$ and ZrO_2 decreases the electronic density in the Zr core displacing at higher binding energies the Zr signals in the XPS studies [7], indicating that a catalyst with attractive acidic properties was generated as shown below. In the ammonia-TPD studies we have taken special care to reduce the lag times in the sample cell and in the pores (large pore size) that tend to interfere with the process profiles, and therefore these effects were negligible. TPD models found in the literature deal with experiments conducted either

under vacuum or under an inert gas stream. The theory previously exposed assumes that ammonia concentration gradients develop within the zeolite pores of the samples during the TPD runs [8]. Considering that we work under N_2 flux and the largest pore sizes of mesoporous Carbon, we suggest that this state is not responsible for the occurrence of the TPD maxima observed in this work. However, free re-adsorption effectively occurs at pretreatment temperatures under 477ºC but desorption is irreversible above this temperature. The total concentration of the acid sites and the concentration of their relative forces were determined by a NH_3-TPD. Regarding the strength of acidic sites, some authors [9, 10], have reported that ammonia desorption signals below 400 ° C correspond to sites with weak surface acidity, while desorption signals are exhibited at temperatures above 400 ° C corresponding to sites with higher acidity. The result is shown in Figure 3c. SMC material does not retain ammonia-showing absence of acidity. The Zr-SMCs catalytic material has a broad peak between 380 and 700 ºC. The value with a maximum at 465 ºC and other around 550ºC was determined by deconvolution of NH_3-TPD spectra. The deconvolution area of the peaks has an experimental error of ± 5 area / g. As a function of TPD, there are 0.94 and 0.86 mmol/g of NH_3 retained, corresponding to the moderate and strong acid sites. The total acidic sites are 1.80 mmol/g, greater than the number of Zr species (1.05 mmol/g) isolated and adhered to the catalyst surface.
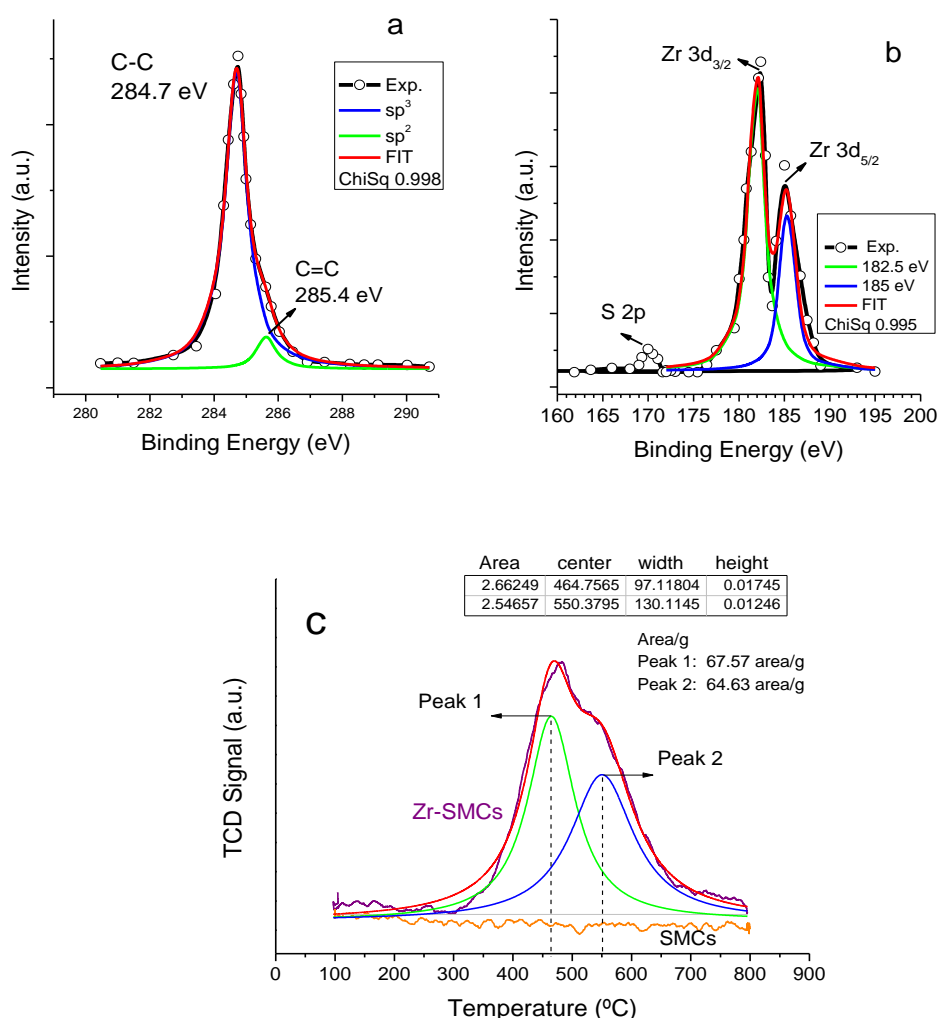

Figure 3. XPS spectra of SMC, C 1s peak deconvolution (a),   Zr 3d peak deconvolution (b) and NH_3-TPD of Zr-SMC (c).

This difference suggests the presence of Bronsted acid sites due to $SO_4^=$ species and Lewis acid sites due to zirconium. In the graphite structure (our XRD studies indicate that SMC has typical graphite carbon planes), and by using XPS of the C 1s peak (Figure 3b), it can be attributed to the hybridized carbon sp^3 and sp^2; the latter are the possible anchorage sites of sulfated Zr species in the walls of SMC. When the atomic S/Zr ratio is greater or around 1, as is our case, 0.9 [12], the existence of a monodentate structural species is proposed (scheme 1).

Therefore, this model implies two acid sites for each monodentate species according to our suggestions from the TPD results, where the total ammonia content retained was higher than the zirconium species in the catalyst. Hence, Zr-SMC catalyst has Lewis and Bronsted acid sites. In the most simple linear π systems, bonding to metals occurs by two interactions. Electron density is donated directly to the metal, as a sigma bond would be formed. In addition, the Zr^{4+} can donate electron density back to the linear π system C=C from the metal's d orbital to the empty π* orbital of C=C of SMC [13]. We are conducting further studies on the true chemical nature of the active sites.

Scheme 1. Proposal of acidic sites and their interaction with the mesoporous carbon support

Conclusions

We have presented a novel synthesis procedure for the formation of solid acid catalysts consisting of mesoporous starch carbon functionalized with sulfated zirconia. During the crystallization process, P123, starch, zirconia and silicon can be co-assembled. After the sulfuric treatments, the physical characteristics of the parent carbon were retained in the final material, showing a large surface area (1300 m^2/g), a large pore volume and a well ordered porosity composed of uniform mesopores of approximately 3.5 nm. Based on experimental data, SMC has successfully anchored sulfated zirconia on its surface. The presence of two high-temperature desorption peaks in the NH_3-TPD profile of the catalyst indicates medium and strong acidic sites in the Zr-SMC catalyst, and can be considered a super acid catalyst.

Acknowledgments

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Oscar Anunziata*
Expertise

Science and Technology expertise: Design, synthesis, characterization, adaptation and modification of microporous and mesoporous nanostructured materials and their carbonaceous replicas (CMK, CNT). Incorporation of active nanospecies. Characterization by instrumental methods and their confrontation with the planned structures. Engineering of the reactions and the processes involved inside the materials. Evaluation of catalytic properties. Redesign of the materials based on the information of the Bulk and the surface of the materials as well as their interaction with reactants, intermediates and reaction products. Incorporation of organic molecular nanowires. Controlled Release of Pre adsorbed Drugs in Nanostructures, Evaluation of application properties in LEDs and conductive and semiconductor composites. Hydrogen reservoirs. Applications