

August 24, 2021

LETTER OF INVITATION TO THE CONFERENCE

To,

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Dear Dr. Anunziata

2021 International Conference on Frontiers of Nanomaterials and Nanotechnology (NanoMT 2021) which will be held in Singapore on October 15-17, 2021. This Conference aims to offer an exciting forum to stimulate in-depth discussions and collaborative work among the participants to advance and broaden the frontier of knowledge in nanomaterials science and engineering.

We are pleased to accept your paper entitled

“Mesoporous Sulfate-Zr-Carbon Nanomaterial: A new chemically active species”

Oscar A. Anunziata* and María L. Martínez

Thank you for your interest in participating in this Congress. We look forward to welcoming you to the congress.

Yours sincerely

Advisory Committee: Daniele Sanvitto— Istituto di Nanotecnologia, Via Monteroni, Italy

Mesoporous Sulfate-Zr-Carbon Nanomaterial: A new chemically active species

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Abstract

In this work, we report the successful preparation of a nanomaterial with acidic properties from sulfated zirconium functionalized mesoporous carbon (SZr-MC). SZr-MC presents a new chemical species formed by bonding Carbon with sulfated Zirconium (Zr): C-O-Zr- H₂SO₄ and C-Zr (H₂SO₄)-C. It has a surface area of approximately 1300 m² g⁻¹, and a total pore volume of 0.94 cm³g⁻¹, composed mainly of mesopores with an average pore size of 3.5 nm. The surface composition and chemical states of the elements did not reveal that ZrO₂ was an isolated cluster. A new nanomaterial based on mesoporous carbons modified with sulfated Zr was developed, which opens up a wide range of acid-catalyzed reactions applied to biomedical engineering.

Keywords: Sulfated mesoporous carbon; SZr-C₂; SZr-O-C interactions; superacid properties.

1. Introduction

Although Zr-sulfate (SZr) has been widely used in industrial reactions, a few carbon-based sulfated zirconia supports have been reported [1-4]. This research reports on our ongoing efforts to advance in the design of an acid catalyst based on carbon nanostructure. Thus, we developed a Zr-MC-based acid catalyst functionalized with sulfated (SZr-MC) with the typical carbon structure of graphite. The

functionalization with sulfated Zr groups leads to the catalyst to exhibit super-acid properties and non-bulky ZrO₂ species. The goal of this work is the incorporation of zirconium, in the process of self-assembly of the template agents (P123) and hydrolyzed TEOS, and starch as a source of carbon in the original synthesis mixture. This direct incorporation of zirconia leads, after carbonization, to ordered mesoporous carbon material, with zirconium in its structure (Zr-MC), and without zirconium oxide as a bulky species. The sulfated mesoporous carbon has high acidity which can make the SZr-MC material a catalyst with superacid properties. We specifically report the characteristics of a new chemical species based on C-O-Zr- H₂SO₄ and C-Zr (H₂SO₄) -C.

2. Synthesis

The synthesis of the materials was performed using starch (as Carbon source), 4.0 g, P123, (Sigma-Aldrich) 8.0 g and 320 mL HCl solution (2 M) was 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 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 of deionized water and 98 wt.% H₂SO₄ (1 mL), under stirring for 12 h, and pre-carbonized at 100 °C for 6 h. The pre-carbonized sample was calcined at 750 °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 Zr-MC material. Mesoporous carbon was functionalized with H₂SO₄ to become sulfated. The newly prepared material was called Zr-MC, containing an atomic S/Zr ratio around 0.98(±0.05) and total zirconia approximately 2.4 ±0.05 mmol/g of the catalysts, calculated on the basis of induced coupled plasma emission analysis (ICP).

2.1 Characterization

SZr-MC sample was characterized by BET, XRD, SEM, TEM, XPS, and FTIR of pyridine (Py). XRD results were acquired using a PANALITYCAL Phillips X'pert XDS diffractometer with a diffractometer beam monochromator and a CuK α radiation source. The BET surface area and pore size distribution of the material was analyzed by nitrogen adsorption using a surface area analyzer (Quantachrome / Autosorb1). Chemical states of the elements of sulfated-Zr-MC identified by XPS acquired on a Microtech Multilb 3000 spectrometer, equipped with a hemispherical electron analyzer and MgK α ($h\nu=1253.6$ eV) photon source. The surface morphology of the SZr-MC was characterized by scanning electron microscopy performed in a JEOL JSM-6610LV Scanning with energy-dispersive X-ray spectroscopy (EDS). The FTIR spectra were obtained from a JASCO 5300 Fourier Transform spectrometer. The pyridine adsorption and desorption studies were conducted in a vacuum line, evacuated at 10^{-4} Torr for 4h, and heating at different temperatures. The samples (self-supported wafers), were first degassed at 400°C for 1 h under vacuum, using a cell with CaF $_2$ windows.

3. Results and Discussions

3.1 XRD-BET-TEM-EDS Studies

The diffraction patterns of the SZr-MC at low- angles shows the main signal around $2\theta = 0.9^{\circ}$ corresponds to plane reflection (100), while the $2\theta \approx 1.4^{\circ}$ is produced from plane reflection (110). The two reflection signals can be assignable to a hexagonal P6mm crystallographic space group. The value of the spacing d was used to calculate the cell parameter a_0 , considering that it is a hexagonal type unit cell, the values of $d_{100}= 10.69$ nm, and the cell parameter is 12.35 nm. At high angles, which can be indexed to the (002) and (100) planes typical of graphite carbons. The material has typical hysteresis

loops with capillary condensation ($P/P_0 > 0.55$) and the pore size distribution ($\cong 3.5$ nm). The hysteresis loops correspond to isotherm type-IV, indicating a mesoporous structure. Elemental mapping of S was found by Energy-dispersive X-ray spectroscopic (EDS).

3.2 FTIR Studies

According to Fig. 1, Zr-MC materials have not retained pyridine from 200 °C in evacuation temperature. Moreover indicate that for each temperature range of evacuation, the number of Bronsted sites is slightly greater than Lewis, finding that above 550 °C, SZr-MC has the most Bronsted sites. The total of acid sites, (that determined after evacuation to 200°C and 10^{-4} Torr for 4h, is approximately 2.36 mmol/g, greater than the number of Zr species (1.16 ± 0.05 mmol/g) content in the nanomaterial. According to the regionalization criteria of the acid strength, described, in WMAS (weak and medium acid sites), SAS (strong acid sites) and SSAS (super strong acid sites), we found that it was distributed in, 0.42, 1.33, and 0.61 mmol/g respectively, having in consideration that the implicit error is ± 0.015 mmol/g.

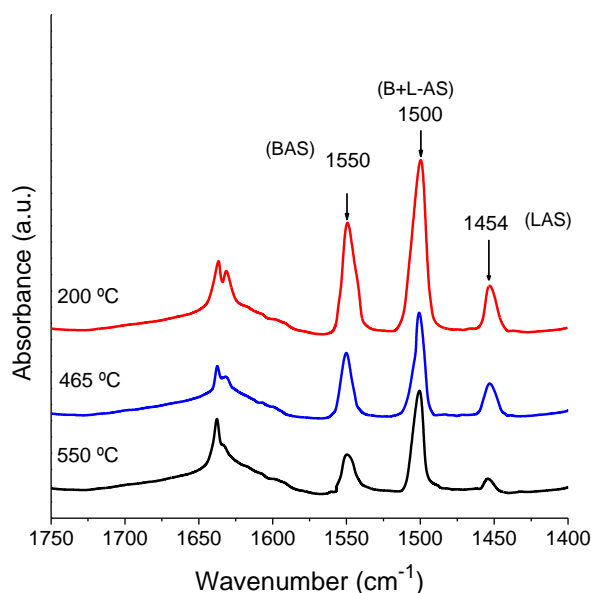


Fig.1: FTIR of pyridine retained at different temperatures on SZr-MC

If we consider the sum of the SAS and SSAS regions, 82% of the sites are strong and only 18% are weak-medium. These results lead us to consider, in addition to the inhomogeneity of acid sites, the existence of at least two types of active species of sulfated Zr-MC, responsible for distributing strength

3.2 XPS studies

The presence of S-O or S=O bonds was indeed verified by XPS (Figure 2). ZrO_2 crystals were not detected, indicating that the material has zirconia interacts with the walls of MC, with the absence of clusters of metallic oxides dispersed on its surface, such as we corroborate with XRD and XPS studies.

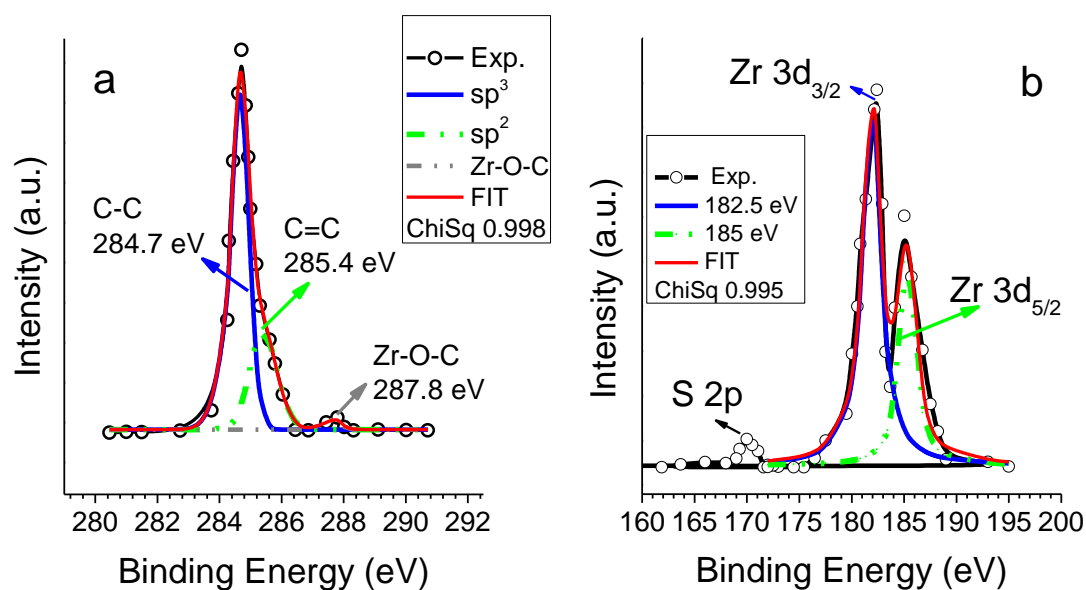


Fig. 2: XPS spectra of MC, C 1s peak deconvolution (a), Zr 3d peak deconvolution (b) of SZr-MC

The C 1s signals are shown in Fig. 2.a, where deconvolution allows us to identify three bonding manners of C. The first peak is attributed to C-C with sp^3 hybridization and the second to sp^2 hybridization characteristic of carbon graphite. It is interesting to observe the binding energy assigned to the Zr-O-C

bond at 287.8 eV [5, 6], without presenting the SZr-MC material, C-OH bonds. In Fig. 1b, the S-O or S=O species attributed to sp^2 appearing as a wide signal near 170 eV. Moreover, the Zr signals ($3d_{5/2}$ and $3d_{3/2}$) which are located around 182.5 eV and 185.0 eV (± 0.2) would not be in accordance with the pure ZrO_2 [7, 8]. It can be inferred that the interaction of SO_4^{2-} and ZrO_2 decreases the electron density in the Zr core shifting to high binding energies the Zr signals in the XPS investigations [9], suggesting that a new and attractive acidic species was generated as illustrated in Figure 3.

About the Zr-C interaction, without the presence of ZrO_2 , we propose a model involving two acid sites for each monodentate species according to our suggestions from Py-FTIR results, where the total acid content was higher than that of the zirconium species in the carbonaceous material. Therefore, SZr-MC has strong Lewis and Bronsted acid sites [10]. Thus in a simpler linear π -system, the binding to the metals would occur by two interactions: the electron density is donated directly to the metal, since a σ

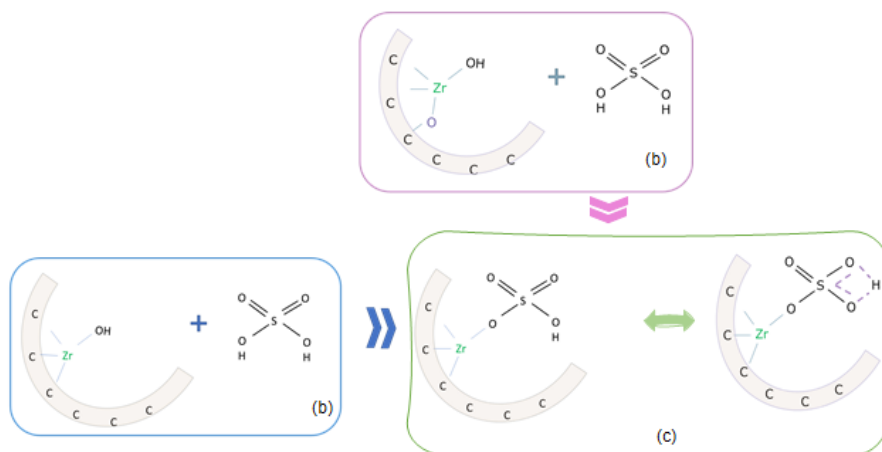


Fig. 3: Proposed new chemical species: mesoporous carbon wall, Zr-C (a) and C-O-Zr (b), and monodentate active site of Zr-C sulfate (c).

bond would be formed, and the Zr^{4+} can donate the electron density back to the linear π C=C system from the d orbital of the metal to the empty π^* orbital of C=C of MC [11], see Fig.3 a.

We suggest that the Zr-O-C bonds could be associated with the high amount of -OH groups in the carbon parent (starch), facilitating the creation of these bonds and facilitating the addition of Zr to the carbonaceous lattice. The SZr-MC material is expected to show the nature and strength of the specific acidic sites. Relying on the above, we might be able to suggest the second type of Zr-mesoporous carbon wall interaction of the MC as C-C-O-Zr (Fig.3 b). Both types of Zr-C and Zr-O-C interactions would conduct to the same kind of sulfated site, the monodentate one (Fig.3 c). The sulfation of zirconia would result in corresponding changes in surface acidity, in respect to Bronsted acidity, creating a new kind of Bronsted acid site, with the likelihood of protons creating multicentric bonds with sulfate anions [12], and the electron-accepting properties of Zr are promoted by the inductive property of the SO_4^{2-} anion, that would remove the electron density of Zr or by activating it chemically by direct activation with the O atom of the sulfate complex.

Our preliminary research results revealed that the SZr-MC nanomaterial possessed clinically relevant cytotoxic activity towards colon cancer cells and suppressed their growth [13]. Moreover, exhibiting an attractive antimicrobial activity both against Gram-positive and Gram-negative bacteria, opening a very encouraging field for their use in a variety of biomedical activities.

Conclusion

We have presented a novel process of formation of a new acidic nanomaterial consisting of mesoporous carbon functionalized with sulfated zirconium. XRD, SEM, TEM and XPS studies indicated the absence of ZrO_2 as a bulk species. Therefore, Zr as an isolated species was successfully anchored directly on the MC for the further sulfation. In addition, supporting evidence from the XPS C 1s data can be ascribed to the sp^2 hybridized carbon (from the graphitic structure of the mesoporous carbon), which would then

form Zr-C bonds. Additionally, the high quantity of -OH groups, originating from the starch used as carbon source, would encourage the generation of Zr-O-C species (also detected by XPS), being part of the MC walls, in the self-assembly process. The evidence of high pyridine retention temperature measured by FTIR indicated medium, strong and super-strong acidic sites in the SZr-MC nanomaterial. These superacid properties are encouraging in biomedical applications.

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