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Super-acid Sulfated/Zirconium-Containing Nanostructured Carbons

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Abstract

In this work, we report the successful preparation of a superacid mesoporous carbon functionalized with sulfated zirconia (SZr-C). SZr-C has a surface area of approximately 1300 m² g⁻¹, and the total pore volume of 0.94 cm³g⁻¹, composed mainly of mesoporous with an average pore size of 3.5 nm. The composition of the surface and the chemical states of the elements did reveal Zr isolated species. According to the data collected by infrared spectroscopy (FTIR), of pyridine desorbed at various temperatures, the total number of acidic sites was 2.36 mmol/g and the distribution in weak- medium, strong and super acidic sites was determined. The activity in the methylation of aniline indicated that the acid sites are strong, and have not redox properties.

Keywords: Sulfated-Zr-Nano- Carbon; catalytic activity.

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1. Introduction

Recently, heterogeneous acid catalysts such as sulfated zirconia [1], and tungsten zirconia [2], and the preparation and characterization of SZr-SMC was reported [3]. The functionalization of Zr-SBA-15, with sulfonic groups in the catalyst increases the acidity in the solid surface. In most of the works, the Zirconia sulfate is found as a bulk of elevated dimensions, (several hundreds of nanometers, so looking for its decrease and thus greater surface area exposed and greater activity of the ZrO₂ crystals to be sulfated, Mishra et al. [4] attempted to nanonize them, reported crystals of sulfated zirconia around 25 nm. This research reports the design of an acid catalyst based on carbon nanostructure. Thus, we developed a SZr-C, 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. The sulfated mesoporous carbon has a high acidity that can make the SZr-C material a catalyst with super acidic properties.

2. Materials and Characterization

The synthesis of materials and the characterization by BET (Brunauer–Emmett–Teller, X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) X-ray Photoelectron Microscopy (XPS), programmed thermodesorption of ammonia (NH₃-TPD) was reported recently by us [5]. To determine the acidity FTIR spectra of pyridine 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 in vacuum, using a cell with CaF₂ windows.

2. Catalytic activity

SZr-C activity was investigated in the gas phase alkylation of aniline with methanol at T °C= 300; Methanol/Aniline= 3 and different conversion levels, obtained by varying the contact time, (based on aniline w/f). The reaction system consisted of a fixed bed reactor constructed of 8mm id 300mm long Pyrex glass, placed in a controlled furnace using a cutting pyrometer. The reagents were introduced into the reaction zone by means of a positional displacement pump. The reaction products were analyzed by gas chromatography, using a 30 m. long AT-WAX capillary column with temperature programming and FID detectors.

3. Results and Discussion

XRD of SZr-C at low-angle shows two signals indexed as reflections (1 0 0) and (1 1 0), respectively. At high angles two broad signals at high angles, which can be indexed to the (002) and (100) planes typical of graphite carbons. By BET typical hysteresis loops with capillary condensation (P/P₀ > 0.55), corresponding to isotherm type-IV, indicating a mesoporous structure was found.

The surface composition and chemical states of the elements indicated C 1s signals. The first peak assigned to C-C with sp³ hybridization and the second with sp² hybridization typical of Carbon Graphite. The interesting aspect is to observe the energy binding attributed to the Zr-O-C link at 287.8 eV [6], without presenting SZr-C material, C-OH bonds. S-O or S=O species 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 ZrO₂ [7]. It can be deduced that the interaction of SO₄²⁻ and ZrO₂ 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.

FTIR studies

The application of Fourier Transform Infrared Spectroscopy (FTIR) is widely known, in the determination of acid sites, using a base, mainly pyridine as a probe molecule. Thus, in Figure 1, we show the spectra of adsorbed pyridine (see experimental section), desorbed in vacuum at various temperatures. The criteria for assessing acidic sites as weak, medium and strong to those sites that retained Py (at 10^{-4} Torr), above 250, 350, and 450 °C, respectively, using H-ZSM-5, HZn-ZSM-5, and InH-BEA, has been reported by us [8]. In this work, we apply as criteria to determine the pyridine evacuation temperatures (Py), the values of the NH_3 -TPD study profiles, despite the difference between the pK_b of both bases. Thus, we start the evacuation at the temperature at which ammonia is observed, in the NH_3 -TPD studies (200 °C), to have a first idea of the total acid sites. The second premise was to evacuate at 465 °C and 550 °C (maximum of the first and second NH_3 -TPD peak, respectively). Thus, knowing the total acid sites, we would arbitrarily infer the acid properties of the material in three categories: weak or medium acid sites (WMAS), strong acid sites (SAS) and super acid or super strong sites (SSAS). The WMAS were calculated as the total Py retained after evacuation at 200°C minus Py retained at 465°C; the SAS as the total Py minus WMAS minus Py retained above 550°C; and the SSAS sites as the quantity of Py retained at more than 550°C (Table 1). Obviously, this study allowed to differentiate Bronsted and Lewis sites for each case and to perform a qualitative and quantitative analysis of the acid properties of SZr-C.

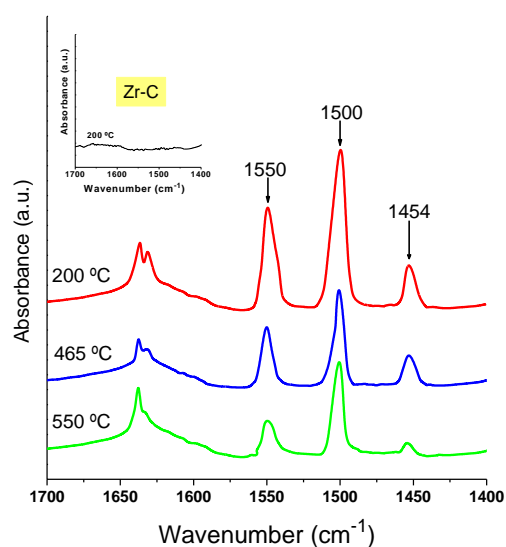


Figure 1 FTIR of pyridine retained at different temperatures on SZr-C

Figure 1 indicates that, as the desorption temperature of Py, pre-adsorbed on SZr-C, decreases the bands attributable to Bronsted acid sites (1550 cm⁻¹), Lewis acid sites (1454 cm⁻¹) and the band of approximately 1495 cm⁻¹ typically assigned to a combined band related to Bronsted and Lewis sites [9]. Simultaneously, it can be observed that the retention of Py over 550 °C (SSAS) is a consequence of Bronsted acid sites, which are 3 times higher than Lewis acid sites, allowing as, a first approximation, to assume that the catalyst provides more Bronsted SSAS. In addition, the inset in Fig. 1 appears in the same study conducted on the material before it was sulfated (Zr-C), and remarkably, but in line with the NH₃-TPD studies, it has no acid sites. Wen-Hua Chen et al. [10] found that pure ZrO₂ samples display only bands in association with the Lewis sites, while Bronsted sites appeared after its sulfation, which would once again substantiate the absence of ZrO₂ as bulky species in Zr-C and SZr-C material. Recently, L. Rivoira et al. [11], have reported only the occurrence of acidic Lewis sites in a Ce-Zr-SBA-15-based catalyst, suggesting its cause in the existence of Zr⁴⁺ isolated into the framework. The amount, nature and strength of acidic sites of the SZr-C catalytic material, acquired by FTIR of Pyridine are listed in Table 1.

Table 1 FTIR data of SZr-C acidic sites as a function of pyridine* retained at different temperatures

Desorption Temp. °C	Py**(mmol/g)		Py**(mmol/g) for regions					
			WMAS		SAS		SSAS	
	BS	LS	BS	LS	BS	LS	BS	LS
200	1.37	0.99						
465	0.98	0.77						
550	0.43	0.18						
			0.25	0.17	0.75	0.58	0.43	0.18
TOTAL	2.36		0.42		1.33		0.61	

*before desorption at 10⁻⁴ Torr for 4 h. **±0.015 mmol/g

According to Fig.1, Zr-C materials have not retained pyridine from 200 °C in evacuation temperature. The data of table 1 indicate that for each temperature range of evacuation, the number of Bronsted sites is slightly greater than Lewis, finding that above 550 °C, SZr-C has 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, slightly less than those obtained by NH₃-TPD (2.49 mmol/g) but greater than the number of Zr species (1.16±0.05 mmol/g) content in the catalyst). According to the regionalization criteria of the acid strength, described, in WMAS, SAS and SSAS, 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. 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-C, responsible for distributing strength. The reason, for which we study in this work, the determination of acidity by both NH_3 -TPD and pyridine FTIR methods, is related to the fact that several authors using similar catalysts have applied one or the other method and it is more difficult to compare the results. For example, recently, L.G.Tonutti et al. [12], examined the acidity of H-ZSM-5, reported a total of 1.4 mmol/g of total acid sites, between 25 °C and 727 °C, but used the temperature of desorption of pyridine, applying similar criteria from us, to the regional distribution of acidic strength. To assess the activity of the catalyst, two catalytic evaluations are presented below that corroborate the strength and nature of the sites determined by Py-FTIR.

4. Activity Studies

Aniline alkylation with Methanol

In previous works, in search of the generation of polyaniline within host channels such as, MCM-41, SBA-15 [13], SBA-3 and SBA-16 [14] (whose weak acidity was demonstrated), we studied aniline adsorption by infrared spectroscopy. We observed that aniline is adsorbed in large proportion by the SBA hosts, through the pi electron system of the aniline, with electron acceptor sites of this material, i.e. the Si-OH groups, leaving free amine groups, which allowed its subsequent PANI polymerization.

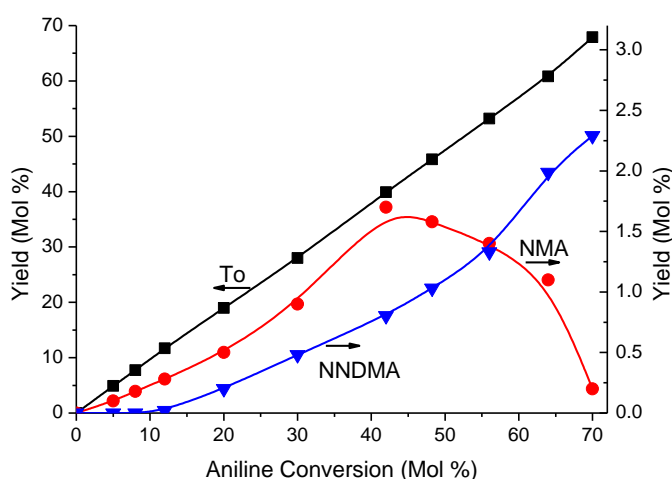


Figure 2 OPE curves of SZr-C: activities (product yields) versus Aniline conversion, extrapolated at zero time and at 380°C.

Thus, in this case, the catalysts with weak acid sites can interact with the aniline similarly giving free amine groups to be alkylated. However, if the acid sites are strong or super acid, the interaction with aniline is through the NH₂- group, leaving the aromatic ring of the aniline free for its potential alkylation. Surprisingly (Fig. 2), when we studied the alkylation of aniline with methanol, a comparative analysis of all reaction products obtained indicates that

*Toluidine is the initial and stable product of aniline alkylation with methanol, with the highest yield and more than 95% selectivity in all ranges of aniline conversion.

* N-Methylaniline (NMA), is primary an unstable product, reaching only at 1.7 mol % at aniline conversion of 42 mol %

* N,N-Dimethylaniline (NNDMA), is derived from NMA alkylation, so it is a secondary stable reaction product, reaching 2.29 mol % to 72 mol % aniline conversion.

- 2,4-dimethylaniline (DMA), 2,3,4-trimethylaniline (TMA), was not produced.

These results corroborate the new SZr-C catalytic material mainly offers sites of strong and very strong acidity. Thus, Toluidine appears as a main product in the entire range of aniline conversions. Furthermore, Figure 2 significantly demonstrates how the low alkylation levels of the amino groups generate low production of NMA and NNDMA [15]. Results are in correlation with TPD and FTIR analysis, and the low proportion of ammonia or pyridine retained below 465 °C, which can be considered to denote medium or weak acid sites, which are active for the alkylation of the NH₂-group of aniline

Nature of SZr - C interaction

At this point in our work, we must ask ourselves a question that we will only try suggesting two answers, to approach this dilemma more effectively.

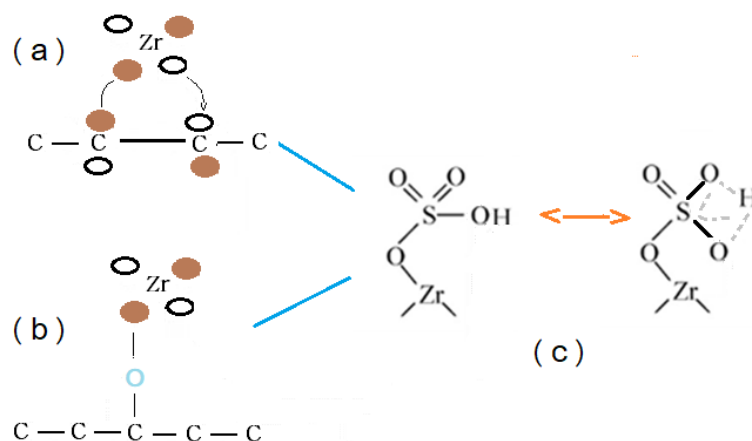
By auto-assembly of hydrolyzed TEOS, P123 and starch, a carbonaceous material after oxidation with sulfuric acid, indicates, the possibility of competition between hydrolyzed TEOS and PEP 123 and the OH groups of starch, generating a hybrid material of Si-C, that then when extracting the silicon, generates SMC, with the presence of -OH stretching vibration sites determined by FTIR. The material does not have zirconium. In this point, the first difference with our SZr-C, is that we do not detect acid sites before sulfation. On the other hand, Ziyuan Zhao [54] used the technique of interstitial carburation to manufacture carbide coatings for zirconium. The coatings showed a microstructure gradient with a volume ratio of ZrC to 100%, and adhesion among the coating and the base was strong, but the material was achieved at more than 1150°C obtaining high-carbon steel and zirconium sheet. In order to do so, a novel self-template technique is suggested to synthesize ZrO₂ (5–10 nm) nanoparticles embedded in carbon (ZrO₂/C). It provides clear evidence to comprehend the catalytic synergy of ZrO₂ and C, and provides a new approach to prepared

encapsulated carbon metal oxides with effective catalysis with light metal hydrogen storage materials. XRD data further confirm that it has been successful in synthesizing ultrafine ZrO_2/C and ZrO_2 nanoparticles.

An alternative to the question, about Zr-C interaction, without the presence of ZrO_2 , is a model involving two acid sites for each monodentate species according to our suggestions from the NH_3 -TPD and Py-FTIR results, where the total acid content was higher than that of the zirconium species in the catalyst. Therefore, the SZr-C catalyst has strong Lewis and Bronsted acid sites. In the simplest linear systems π , bonding to metals occurs by two interactions. The density of the electrons 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 system π C=C of the orbital d of the metal to the orbital π^* empty of C=C of nano structured C, see Scheme 1a.

Amin Osatiashtiani [16], study by XANES, the interactions of ZrO_2 on SBA-15 and SZr-SBA-15, arriving to the fact that, the tetragonal ZrO_2 contains two not equivalent tetrahedral ZrO_4 units, with different lengths of Zr-O linkage, either in sulfated or non-sulfated materials. The load sharing of the local Zr surroundings is awaited to follow its covalent union to the SO_4^{2-} assemblies.

A signal at 287.8 eV attributed to Zr-O-C was detected by XPS. We suggest that Zr-O-C bonds could be related to the large amount of -OH groups in the carbon source (starch), which would facilitate the formation of such bonds and incorporate Zr into the carbonaceous network. SZr-C material should exhibit the nature and strength of specific acidic sites. Based on the aforementioned, we can suggest a second type of Zr-wall mesoporous carbon interaction, as C—C—O—Zr (Scheme 1b).



Scheme 1 Proposed Zr-wall of mesoporous carbon, Zr-C (a) and C-O-Zr (b), Zr sulfate monodentate active site (c)

Both types of Zr-C and Zr-O-C interactions, would conduce to the same type of sulfated site, the monodentate type (Scheme 1c). The sulfation of zirconia would cause the subsequent changes in surface acidity, with reference to Bronsted acidity, generating a new type of Bronsted acid sites, (with the possibility of protons creating multicentric links with sulfate anions), and the electron acceptance properties of Zr are potentiated by the inductive power of the SO_4^{2-} anion, which would withdraw the electron density from Zr or by its direct activation with the O atom of the sulfate complex.

Conclusion

We have presented a novel synthesis procedure for the formation of solid acid catalysts consisting of mesoporous carbon functionalized with sulfated zirconia. The evidence of high pyridine retention temperature determined by FTIR revealed medium, strong and super-strong acid sites on the SZr-C catalyst, and it can be assumed that these sites correspond to a super acid catalyst. Catalytic evaluations in the alkylation of aniline with confirm the acidic properties of the SZr-C material.

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