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Important Announcement

Due to global impact of COVID-19 outbreak, we will be conducting a webinar of this conference, so that all the attendees can see the proceedings of this event online. A webinar of this event will be conducted on July 22-23, 2020

SESSION Advanced nanomaterial

MESOPORE CARBON STARCH WITH ACID PROPERTIES: SYNTHESIS AND CHARACTERIZATION

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Abstract

We have shown that a promising material with acidic properties can be successfully prepared from starch mesoporous carbon (SMC), functionalized with sulfated zirconia. The process of assembling P123, starch, zirconia, and silicon synthesized Zr-modified ordered mesoporous carbon. SMC and Zr-SMC were characterized by BET for their texture properties and, using Scanning Electron Microscopy (SEM), their morphology. Acidic properties were acquired by programmed thermodesorption of ammonia (NH_3 TPD). These studies show that the Zr-SMCs material is mainly composed of mesopores with an average pore size of approximately 3.5 nm, high surface area and pore volume, and has medium to strong acidity properties.

1. Introduction

Starch Mesoporous carbon (SMC) has attracted attention as a new material due to its applications as drug carrier, catalyst support and energy storage medium [1]. Starch is a non-toxic 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 carbons with lots of hydrophilic groups, which can be widely functionalized in different applications. On the other hand, there is a growing interest in the use of renewable carbon sources for biofuel production. The carbohydrates available in biomasses are very promising resources because they are the main source of natural carbon, renewable and relatively economical [2]. Many researchers have been working with homogeneous acids in the dehydration reaction of fructose in Hydroxymethylfurfural (HMF), but heterogeneous acid catalysts have been revealed to be better. Some of the recently reported heterogeneous acid catalysts are sulfated zirconia [3] and zirconia with tungsten [4]. The functionalization with sulfonic groups in the catalyst increases the acidity in the solid surface. Thus, Brönsted acid sites are found in a more available way, improving the selectivity to HMF in fructose

dehydration [5]. In this research, we developed acid catalysts based on SMC and functionalized with sulfated zirconia.

2. Experimental

The synthesis of materials was carried out according to the literature [6]: 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 (Si/Zr= 20 ratio) were added to the synthesis solution. After stirring for 24 h, the solution was placed in oven for 24 h at 100 °C without further stirring. The material previously washed was dried at 35 °C in 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 the SMC material. Mesoporous carbon was functionalized with H_2SO_4 to become sulfated. The new material prepared was called Zr-SMCs. X-ray diffraction results were acquired using a PANALITYCAL Phillips X'pert XDS diffractometer with a diffractometer beam monochromator and a CuKα radiation source. The BET (Brunauer–Emmett–Teller) surface area and pore size distribution of the material were analyzed by nitrogen adsorption using a surface area analyzer (Quantachrome / Autosorb1). The morphology of the surface of mesoporous materials was characterized by scanning electron microscopy (SEM) obtained using JEOL JSM-6610LV and acidic properties by thermodesorption of 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 NH_3 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

3. Results and Discussion

During the preparation process, P123, starch and silicon and zirconium can self-assemble, at temperatures and times of around 100ºC and 24 hours [6]. The reaction time is very important (less than or greater than 24 hours) and higher temperatures appear poorly assembled or dreadful in the structure, reducing the surface area and the size of the pores (see Table 1).

Figure 1 shows the diffraction patterns of SMC: at low-angle and inset at high-angle. At low- angles, two signals are observed that can be indexed as reflections (1 0 0) and (1 1 0) respectively. Both signals can be associated with the hexagonal symmetry of p6mm. 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 pore structural parameters of Zr-SMCs are given in Table 1. The material is principally composed of

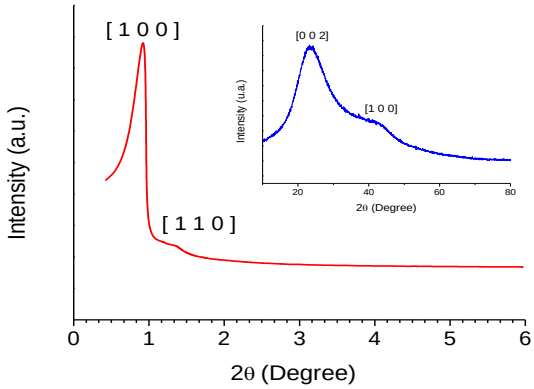

Figure 1: Low-angle X-ray diffraction and inset at high-angle of SMC

mesopores with average pore size about 3.5 nm. It possesses a surface area as high as 1300 $m^2\ g^{-1}$, its total pore volume are 0.94 $cm^3\ g^{-1}$. SEM (Fig. 2a) analyzed the morphology and structure of the prepared material. There are numerous uniform macropores on the surface of the materials, characteristic of mesoporous carbon.

Table 1. Structural properties of the Zr-SMCs sample

Sample	S_{BET} ($m^2\ g^{-1}$)	Volume total ($cm^3\ g^{-1}$)	Mean pore diameter (nm)
Zr-SMCs	1301	0.94	3.5

Fig. 1b shows the typical hysteresis loops with capillary condensation (P/P0 > 0.55) of Zr-SMCs. The hysteresis loops correspond to isotherm type-IV indicating mesoporous structure. The hysteresis loops of SMCs show H3 characteristics, which can be attributed to slit-shaped pores. The surface acidity of the catalysts have an important role in improving catalytic processes. The total concentration of the acid sites and the concentration of their relative forces, the ammonia desorption was determined with a programmed temperature. About the strength of acidic sites, some authors [8,9] have reported that ammonia desorption signals below 200 ° C correspond to sites with weak surface acidity, while desorption signals exhibited between 200-400 ° C are associated with acidic sites of medium strength, and the signals found at temperatures higher than 400 ° C correspond to sites with strong acidity. The total amount of acidic sites was obtained by NH_3-TPD. The result is shown in Fig. 3. The SMC material does not retain ammonia showing absence of acidity. The catalytic material Zr-SMCs has a well-defined peak between 480 and 550 ºC, characteristic of moderate to strong acidity. Therefore, we can infer that the number of acid sites (according to the TCD signal), and their strength are related to the number of sulfated Zr species isolated and adhered to the carbon-carbon surface of the catalyst.

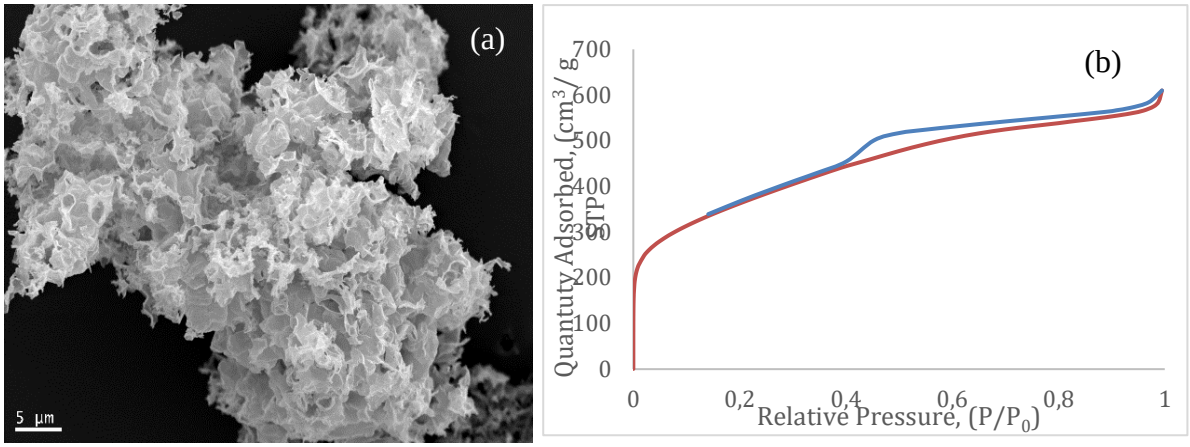

Figure 2. (a) Scanning electron microscope (SEM) image and (b) BET Isotherm of Zr-SMCs

In the structure of graphite (our XRD studies indicate that SMC has typical planes of graphite carbons), two electrons form two single bonds (σ), while the other pair forms a double bond (π bond), the latter being the possible ones anchorage sites of sulfated Zr species to the walls of SMC. We are conducting further study on the true chemical nature of active sites.

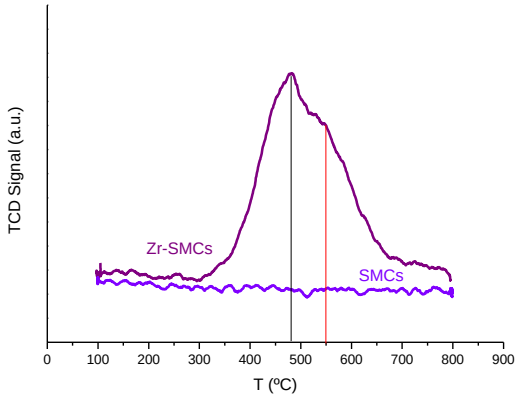

Figure 3. NH_3-TPD of SMCs and Zr-SMCs

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 [10]. Considering that we work under N_2 flux and the largest pore sizes of mesoporous Carbon, we suggest that this state is responsible for the occurrence of the TPD maxima observed in the present work. On the other hand free re-adsorption effectively takes place at pretreatments temperatures under 477ºC but that desorption is irreversible above this temperature.

4. Conclusions

We have presented a novel synthesis procedure for the formation of solid acid catalysts consisting of a SO_4^{2-}/ZrO_2 functionalized starch mesoporous carbon. During the crystallization process, P123, starch, zirconia and silicon can co-assemble. After sulfuric treatments was made, the physical characteristics of the parent carbon were retained in the final material, showing a high surface area (1300 m^2/g), a large pore volume and a well-ordered porosity made up by uniform mesoporous. We show the results the analysis of TPD of NH3, in this study, we observed the presence of two desorption peaks in the NH3-TPD profile of catalyst, the peaks correspond to medium-strength acid sites.

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