

# Preparation of a Solid Catalyst by Sulfonation Superacids from Mesoporous Carbon Material

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## ABSTRACT

A new solid super acid catalyst was functionalized using H<sub>2</sub>SO<sub>4</sub> as catalyst supports a mesoporous carbon from tire rubber. The method of sulfonation in liquid phase was through direct immersion incipient coal 98.3 % concentrated H<sub>2</sub>SO<sub>4</sub> in a flask under reflux. The carbonization temperature of tire rubber pyrolysis was performed with a flow of N<sub>2</sub> at low temperature to obtain a mesoporous carbon and achieve effective sulfonation. The mesoporous carbon was functionalized with the group -SO<sub>3</sub>H, CMHL520, was characterized by XRD, SEM, EDS, IR and elemental analysis, indicating the presence of polycyclic disordered carbon plates in structure extremely high surface area and large pores that provided more acidic surface sites. The high catalytic activity and stability of this catalyst is related to the acid site density by -OH, Bronsted acid sites, hydrophobicity preventing hydration of hydrophilic -OH and -SO<sub>3</sub>H functional groups.

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*Keywords:* Solid super acid catalyst, mesoporous carbon, pyrolysis



## **1. Introduction**

The discovery of mesoporous materials with high surface area and pore volumes different in structure, has opened new opportunities for the conversion of large molecules from the catalytic point of view, as they are very applicable in the petroleum industry, pharmaceutical and Industrial [1]. Today is very important catalytic processes employing heterogeneous phase, as an alternative to the traditional homogeneous processes where the use of catalysts such as sulfuric acid, hydrochloric acid and p-toluenesulfonic acid [2] acid is involved.

Activated carbon is a solid material prepared artificially, which is characterized by a well developed pore structure, which gives a high specific surface area and adsorption capacity. [3] It has great versatility due to the possibility to modify and control the size and distribution of pores in the carbonaceous structure and the chemical nature of the surface during the process of preparation [4].

In terms of chemical composition mainly consists of carbon atoms, about 87-97%. The remaining composition includes hetero atoms such as hydrogen, oxygen, sulfur and nitrogen from the feedstock, or incorporated during the preparation process [5].

Its structure consists of graphite microcrystals, formed by a number of aromatic rings as the interlocking structure of graphite, and forming from 5 to 15 layers of graphitic planes with a spacing of 3 to 4 Å therebetween. Aromatic carbon sheets interconnected appear irregularly and randomly, so that not appear perfectly parallel, or even overlap each other [6]. The interstitial spaces between the sheets aromatic result in pore formation, structural defects, unpaired electrons and holes in the system at the edge of the basal planes. In the presence of hetero-atoms in the reaction medium (sulfur, nitrogen, hydrogen and molecular oxygen), can be formed on said active surface groups [7] centers.

Both the random ordering of the layers as the crosslinking prevents the rearrangement of the structure for graphite, even when this material is heated to 3000 °C. This is the characteristic of activated carbon that contributes most to its most important property, the highly developed internal pore structure and accessible for adsorption processes [8].



With the above it was decided to prepare a carbon rubber trowel amorphous mesoporous type for use as a catalyst support and funcionalizarlo with sulfonic groups to obtain a solid catalyst super acid (CMHL520), in order to carry out a more efficient and environmentally friendly processes used esterification and transesterification of vegetable oil.

Activated charcoal (CMHL) was obtained by a pyrolysis process from tire rubber fiber. The method obtained from this material was developed at the Technologic Institute of Aguascalientes of subjecting tire rubber fibers at high temperatures in an atmosphere of  $N_2$  obtaining a carbonaceous material.

As a method of functionalization of CMHL sulfonation with  $H_2SO_4$  was used. For the sulfonation procedure by which  $-SO_2OH$  sulfonic group is introduced as sulfonating agent using concentrated sulfuric acid was performed 98.3%. It is noteworthy that the sulfonation is called when a carbon atom, or sometimes to a nitrogen atom is attached to the sulfonic group  $-SO_2OH$  [9].

To characterize the CMHL and CMHL520 the following methods were used: Infra Red Spectroscopy Fourier transforms (FTIR), X-ray diffraction (XRD), scanning electron microscopy and EDS.



## **2. Experimental**

### *2.1 Obtaining CMHL from used tire*

- a) A thermal pyrolysis which weighed 5 g sample of tire rubber powder in an analytical balance was used.
- b) The powder was packed into a micro-reactor of stainless steel, once inside the sample in the micro-reactor, purged with N<sub>2</sub> for 10 min before starting the stage of pyrolysis.
- c) In pyrolysis followed rubber which was maintained at a temperature of 515 °C, with a pre-heating ramp of 15 °C / min and N<sub>2</sub> flow of 30 ml / min for 2 hours was begun.

### *2.2 Activation CMHL*

This pyrolysis process consisted of heating at a temperature of 520 °C in an inert nitrogen atmosphere, to break the bonds between the carbon atoms. Thus, the material is dehydrated and the volatiles are removed, increasing the proportion of carbon atoms and forming a carbonaceous amorphous structure when the hydrocarbon chains lose their hydrogen atoms.

Because the energy provided during the heating process, graphite microcrystals are rearranged into the structure recombined together irregularly and joining the aromatic rings to form graphitic planes, creating free interstitial voids that are blocked as a result of the decomposition and deposition tar. During the carbonization step, the lower the heating rate increases the performance for the materials used.

### *2.3 Sulfonation of CMHL*

- 10g were taken of each catalytic support and 100 ml of concentrated H<sub>2</sub>SO<sub>4</sub> (98.3%) of solution. Each was placed in a flask of 500 ml and a temperature controlled around 120 °C.
- The mixture was kept under reflux and stirring for 5 hours as shown in Figure 3.3.



- After treatment, the suspension was washed with hot deionized water at 80 ° C to remove any physically adsorbed species to be detected non-sulfonated ion water seepage. That is to have a neutral pH.
- After filtration, the sample was dried at 120 °C for 8 hours to obtain a sulfonated coal or alternatively, the CMHL520 material.



### 3. Results and discussion

The catalyst support CMHL and CMHL520 catalyst were characterizing by various techniques and the results are shown below:

The FTIR spectra of CMHL showed in the Table 1 a first peak located at 653 cm<sup>-1</sup> with a weak intensity corresponding to the functional group C-S, the second at 866 cm<sup>-1</sup> with strong intensity corresponding to the aromatic moiety HCC, the third 1140 cm<sup>-1</sup> with a weak intensity corresponding to the asymmetric S=O functional group, the fourth at 1420 cm<sup>-1</sup> with a strong asymmetric stretching intensity corresponding to the aromatic functional group C-C, the fifth and last at 1636 cm<sup>-1</sup> medium intensity corresponding to the functional group C = C.

**Table 1. FTIR of the CMHL**

Bands (cm-1)	Functional group		Allocation	Intensity of the peak in the spectrum
653	C-S	Sust. Para	Elongation	Weak
866	HCC	Aromatic	Elongation	Strong
1140	S=O	Asymmetric	Elongation	Weak
1420	C-C	Aromatic	Symmetric stretch	Strong
1636	C=C	Aromatic	Elongation	Medium
2829	CH <sub>2</sub> /CH <sub>3</sub>		Elongation	Medium



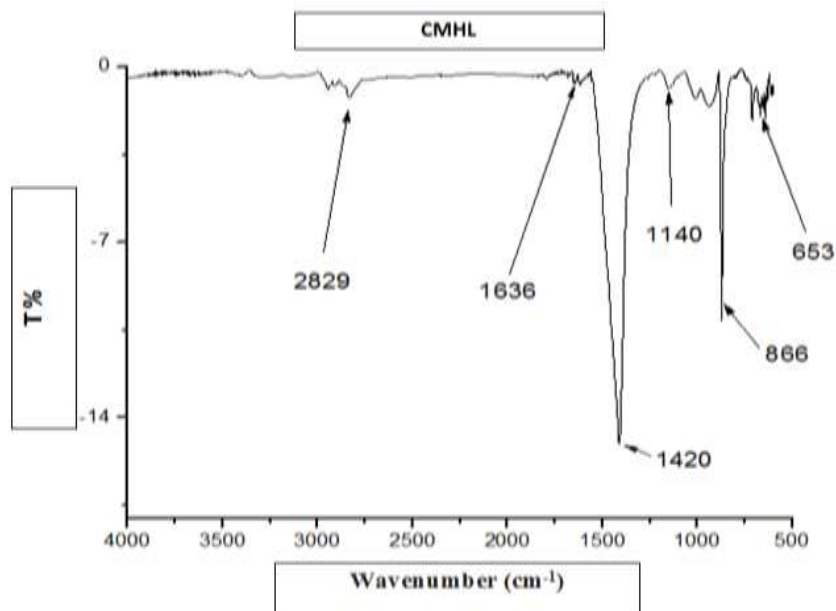


Figure 1. FTIR of the CMHL

The FTIR spectra showed CMHL520 in the Table 2 a first peak located at 617 cm<sup>-1</sup> with a weak intensity that corresponds to the S-OH functional group, the second at 642 and 726 cm<sup>-1</sup> with an average intensity which corresponds to the aromatic moiety C-H the third at 1254 cm<sup>-1</sup> with a weak intensity corresponding to the functional group to the fourth Aromatic C-C 1074 cm<sup>-1</sup> with strong intensity corresponding to asymmetric-SO<sub>3</sub>H functional group, the fifth to 1447 cm<sup>-1</sup> with strong intensity asymmetric stretching corresponding to aromatic C = C functional group, the sixth and last at 1717 cm<sup>-1</sup> with an average intensity that corresponds to the functional group conjugated C = O.



**Table 2. FTIR of the CMHL520.**

Bands (cm <sup>-1</sup> )	Functional group		Asignación	Intensidad del pico en el espectro
617	S - OH	Sust. Para	Elongation	Weak
726 - 642	C - H	Aromatic	Elongation	Medium
1074	SO <sub>3</sub> H	Asimétric	Elongation	Strong
1254	C-C	Aromatic	Symmetric stretch	Weak
1447	C=C	Aromatic	Symmetric stretch	Strong
1717	C=O	Conjugate	Elongation	Medium

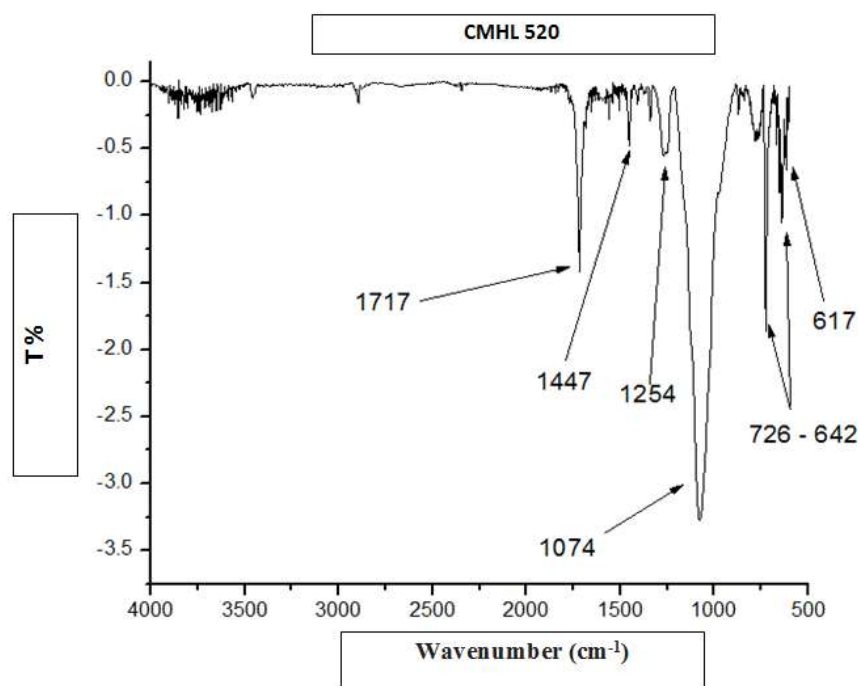


Figure 2. FTIR of the CMHL520.





The XRD diffractogram of CMHL shows the presence of calcite in the activated carbon zincita as shown in Figure 3, and two characteristic peaks at  $2\theta$  angle of  $10-30^\circ$  and  $35-50^\circ$  attributed to the plates amorphous carbon as shown in Figure 4. These results indicated the presence of polycyclic aromatic carbon sheets in the activated carbon of tire rubber.

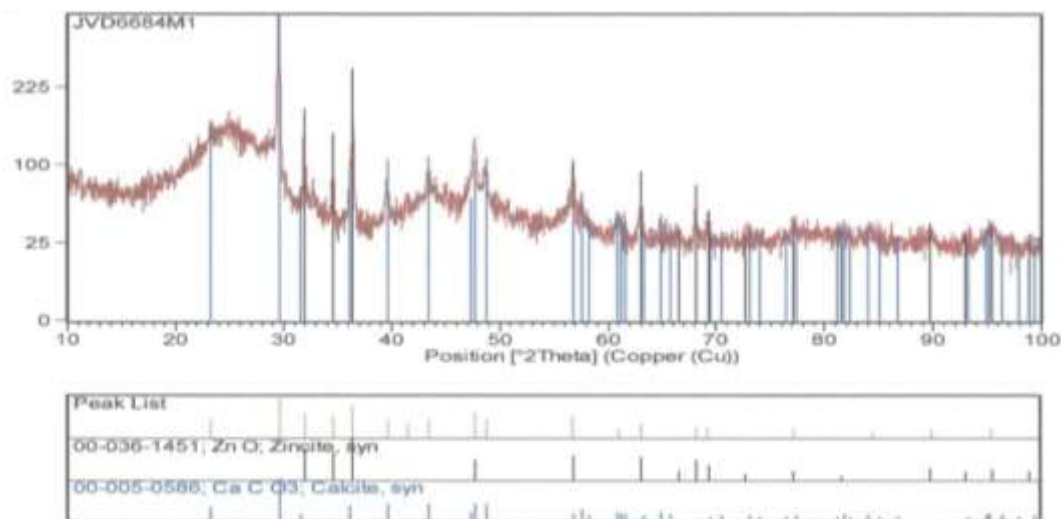


Figure 3. XRD of the CMHL

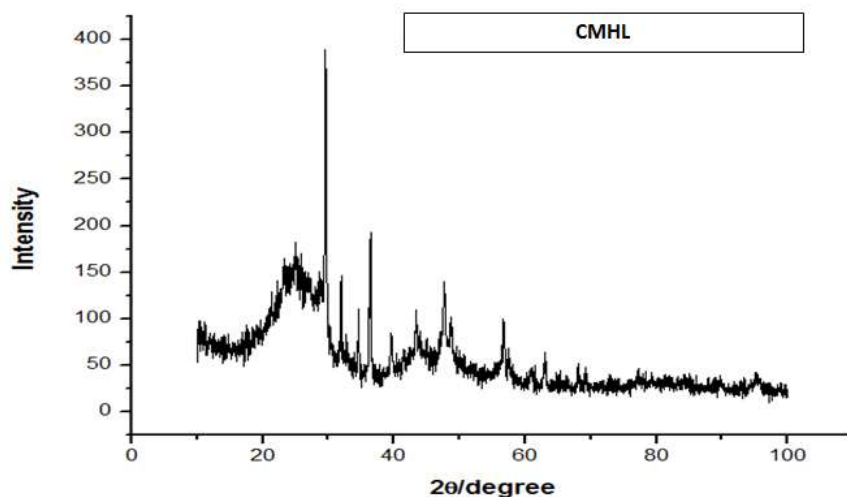


Figura 4. XRD of the CMHL



The XRD diffractogram of CMHL520 not already detected the presence of calcite in CMHL520 zincita as shown in Figure 5, this is attributed to the removal by the contact with sulfuric acid. In Figure 7, the presence of two characteristic peaks shown at the  $2\theta$  angle of  $10-30^\circ$  and  $35-50^\circ$  attributed to amorphous carbon plates. These results indicated the presence of polycyclic aromatic carbon sheets in CMHL520.

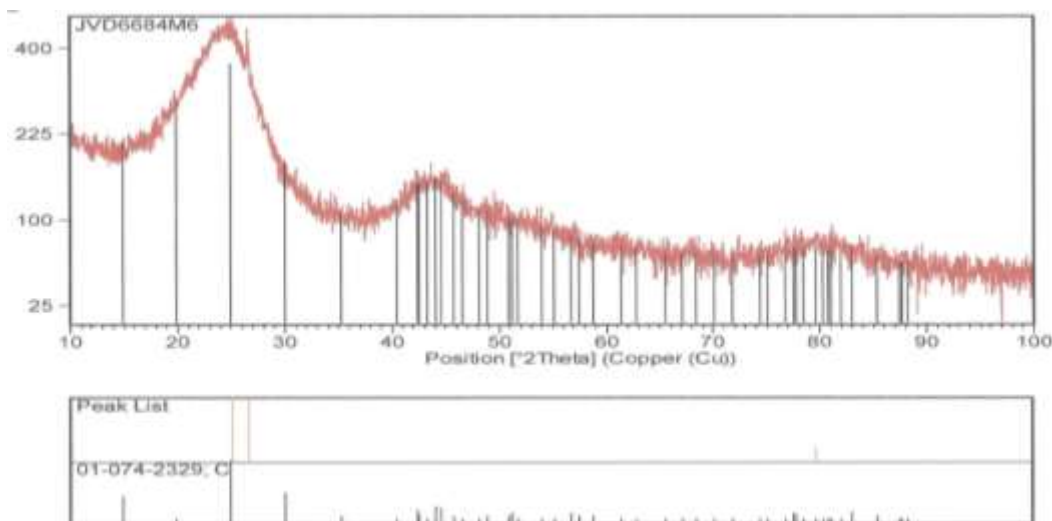


Figure 5. XRD of the CMHL520.

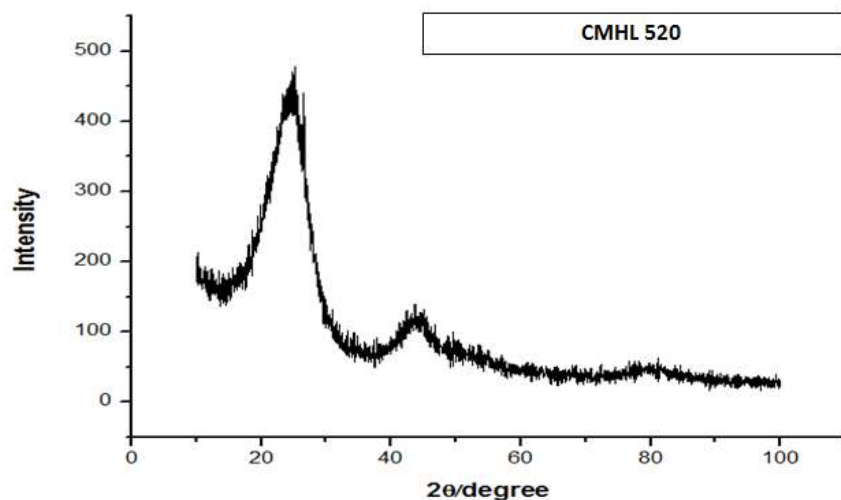


Figura 6. XRD del CMHL520.



EDS analysis to CMHL and CMHL520 was conducted to determine its chemical composition wherein the percentage by weight and the atomic percentage demonstrated an increase in the amount of sulfur in the catalyst. In the Table 3 was observed on the catalyst support a weight percentage of 1.78% of sulfur and on the catalyst was observed by weight percentage of sulfur of 3.82%, which shows increase in sulfur in the coal sulfonated with sulfuric acid. There are 3 sulfur atoms attached to the surface per 200 carbon atoms in the latter case.

**Table 3. Elements in the CMHL and CMHL520.**

<b>Catalyst</b>	<b>C</b>		<b>O</b>		<b>S</b>	
	Wt %	At %	Wt %	At %	Wt %	At %
<b>CMHL</b>	62.29	74.19	21.46	19.19	1.78	0.79
<b>CMHL520</b>	92.09	95.34	4.09	3.18	3.82	1.48

Quantification of acid functionalization CMHL and CMHL520 held by acid-base titration by titration, resulting in a density of acidic groups of 0.92 mmol / g 2.82 mmol / g, respectively, which are anchored in the layer carbon.



#### **4. Summary and perspectives**

The technique used for the sulfonation of the carbon catalyst support tire rubber was performed correctly and that the deposition of sulphone ion was found in the catalytic carbon support for tire rubber from concentrated sulfuric acid.

With the techniques used in the characterization and CMHL520 CMHL are satisfactory and that obtaining a solid catalyst were demonstrated by sulfonation super mesoporous acid from a carbon rubber tire.

CMHL520 with obtaining a density of acidic groups of 2.82 mmol / g the proper functioning in the esterification and transesterificación of vegetable oil used in an autogenous reactor is guaranteed.

#### **5. Acknowledgements**

Thanks to Dr. Javier Rodríguez Varela CINVESTAV Saltillo Unit for their support in the characterization of materials.

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