

Mesoporous Carbon as effective and sustainable catalyst for fine chemistry

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Abstract

It is well known that activated carbon with well-developed porosity is a promising material that have been used for several applications, from adsorption to catalysis. Research in this field has intensified in recent years, looking for new and improved characteristics and applications. Our research group, recently renamed Materials for Adsorption and Catalysis group (MAC) in LAQV-REQUIMTE, has also devoted many research work in this subject, and has developed several collaboration works with other national and international research groups in the field.

Among our research group interests there is the study of catalytic properties of carbon materials and specifically mesoporous carbon. Some of the promising results were selected and summarized here, demonstrating that mesoporous carbon is an efficient and environmentally friendly heterogeneous catalyst.

Resumen

Es conocido que el carbón activado por su desarrollada porosidad es un material prometedor para varias aplicaciones, desde la adsorción a la catálisis. La investigación en este campo se ha intensificado en los últimos años, en busca de nuevas y mejoradas características y aplicaciones. Nuestro grupo de investigación, recientemente rebautizado grupo de materiales para la adsorción y catálisis (MAC) en LAQV-REQUIMTE, también ha dedicado muchos trabajos de investigación en este tema, y ha desarrollado varios trabajos en colaboración con otros grupos de investigación nacional e internacional.

Entre los distintos intereses de investigación de nuestro grupo se encuentra el estudio de las propiedades catalíticas de materiales de carbono y específicamente, de carbones mesoporosos. Algunos de los resultados más prometedores han sido seleccionados y se resumen aquí. Estos demuestran que el carbón mesoporoso es un catalizador heterogéneo eficiente y respetuoso con el medio ambiente.

1. Introduction

Countless of our daily consumed products are obtained resorting to catalytic procedures. Many of the catalysts traditionally employed in those processes show disadvantages such as high reaction temperature, prolonged reaction time, non-catalytic nature of the reagent, low conversion and low regioselectivity. Furthermore, in homogenous phase, other problems may occur dealing with the separation, isolation and purification of the product.

Thus, the development of new and less expensive heterogeneous catalysts and their application in reactions with synthetic interest remains an important challenge. In fact, in recent years, heterogeneous catalysts [1- 3] and among them activated carbon [4-8], have attracted much attention as catalysts in the scope of green chemistry for fine-chemical synthesis.

Activated carbon is an extremely environmental friendly material with a very interesting porous structure that, depending on the precursor and preparation method, is very tuneable. Also this material present enormous versatility and high chemical and physical stability. As such, activated carbons with microporous structure have been employed successfully in several catalytic reactions [9-11]. However, mesoporous carbon with a different porous structure presenting meso and macro porous [12] may result in more efficient catalysts in terms of selectivity towards products among other advantages.

These mesoporous carbons are carbon gels that can be obtained through different procedures and display very interesting features about their structural characteristics, because they are very sensitive to the conditions used during gel synthesis and processing [13].

Resorcinol-formaldehyde (RF) aqueous gels are among the most studied systems [14]. Several thermal and chemical processes can be used to tailor the porous structure and the type and concentration of specific oxygen surface groups.

Carbon xerogels discussed here were synthesized by polymerization of resorcinol and formaldehyde. The surface of the activated carbon was oxidized in liquid phase with HNO_3 and then functionalized with H_2SO_4 . The materials were tested in several acid catalyzed reactions with great success, such as the alcoholysis and aminolysis of epoxides, and the methoxylation of α -pinene.

2. Experimental

The mesoporous carbon samples were prepared according Lin and Ritter [14] by sol-gel technique. All reagents and solvents used in the preparation of resorcinol/formaldehyde aqueous gels and surface functionalization of the carbon xerogels were purchase from Aldrich and used as received.

An aqueous solution of resorcinol (R), formaldehyde (F) and sodium carbonate (C), was prepared in such a way that the solid material is 5% (wt./v) of the total volume, and in which the R/F mole ratio was fixed at 1:2 and the R/C mole ratio was fixed at 50:1.

The initial pH of the solution was adjusted to 6.10-6.20

with diluted HNO₃. The solution was sealed in a flask and magnetically stirred during 1 h. This procedure was followed by a thermal treatment at 85 ± 3 °C during a week, without stirring. The gel obtained was washed with acetone for 3 days. Afterward it was dried under N₂ atmosphere in a tube furnace using a heating rate of 0.5 °C/min. The temperature was heated up to 65 °C and then held there for 5h, followed by a raise until 110 °C and kept there for another 5h. Finally, the carbon xerogel was form by pyrolysis of the dried gel at 800 °C for 3h in a N₂ atmosphere with both heating and cooling rates set at 0.5 °C/min (CM).

For the oxidation of the carbon surface, the carbon xerogel (CM), was refluxed with a nitric acid solution (13M) for 6h (1 g/20 mL). After cooling the materials were washed with deionized water in soxhlet until neutral pH and then dried in oven at 110 °C, thus obtaining the catalyst **CMN**.

The introduction of sulfonic groups in the carbon xerogel surface was achieved by placing the oxidized mesoporous carbon (**CMN**) in a concentrated sulfuric acid solution (1g of CMN/20 mL sulfuric acid solution) and heat it at 150 °C for 13h under N₂ atmosphere. The obtained catalyst was washed with deionized water in soxhlet until pH 7 and then dried in oven at 110°C (carbon **CMNS**).

The different mesoporous carbons were characterized after the oxidation of the surface to determine the features of the catalysts. Some characterization of the parent carbons before oxidation was also performed as a means of comparison. Chemical and textural characterization was obtained by elemental analysis, pH_{pzc}, TPD, BET and XPS.

3. Results

3.1 Carbons characterization

Although different batch of synthesized carbon gels may present slightly different overall values, the preparation of this material and subsequent surface modification treatments are very reproducible. [5-7]

Table 1 shows the textural characterization of the carbon samples for one of such batchs. According to IUPAC nomenclature, the synthesised carbons present a nitrogen adsorption-desorption isotherm type IV with a type H3 hysteresis loop, typical of materials with mesoporosity [15].

Table 1. Textural properties. Adapted from [7].

| Catalyst | S _{BET} (m ² g ⁻¹) | V _{micro} (cm ³ g ⁻¹) | V _{meso} (cm ³ g ⁻¹) | V _T (cm ³ g ⁻¹) | D _p (Å) |
|-------------|---|--|---|--|-----------------------|
| | <i>B.E.T.</i> | <i>t Method</i> | <i>DFT Method</i> | <i>Gurvitch</i> | <i>BJH method</i> |
| CM | 771 | 0.18 | 0.50 | 0.76 | 65.4 |
| CMN | 760 | 0.19 | 0.32 | 0.59 | 51.6 |
| CMNS | 797 | 0.20 | 0.51 | 0.79 | 74.5 |

Table 2. Surface chemistry characterization. Adapted from [7].

| Sample | O/C | O/C | Total Oxygen | pH _{pzc} |
|-------------|------------------------------|--------------------------------|----------------------------|-------------------|
| | <i>XPS</i> (atomic ratio) | <i>E. A.</i> (atomic ratio) | <i>E. A.</i> (atomic %) | |
| CM | 0.06 | 0.075 | 6.3 | 9.7 |
| CMN | 0.20 | 0.25 | 16.0 | 3.2 |
| CMNS | 0.19 | 0.29 | 20.2 | 2.4 |

The textural properties of the mesoporous carbon reveal that the oxidation of the carbon with nitric acid (CMN) had no meaningful effect on the BET surface area, but some decrease of the mesoporous volume is observed. This may be due to the presence of functional groups in the entrance of the pores blocking the accessibility.

On the other hand, the posterior treatment with concentrated sulphuric acid resulted in a material with differences in the pore size distribution, probably due to the formation of new pores and the widening of existing pores by the acid.

The surface chemistry was characterized by TPD-MS, elemental analysis, XPS and pH_{pzc} and the main results are summarised in Table 2.

It is possible to conclude that the surface oxidation with HNO₃ was successful as the samples present a higher amount of oxygen and a lower value of pH_{pzc}. By XPS it was possible to detect sulfonic groups in the surface of sample CMNS, indicating that the introduction of these functional groups was also successful and these are probably the groups responsible for the increase in acidity reflected in the pH_{pzc} value.

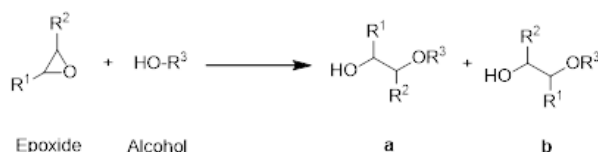
The results obtained with TPD are in quite accordance with the XPS and AE analysis. After oxidation with HNO₃ the samples present a pronounced increase in the functional group content and the most abundant functionalities are phenols and carboxylic groups,

An interesting observation from TPD results is that the carbon functionalised with sulfonic groups (CMNS) exhibits smaller amount of carboxylic acids, this fact supports the conclusion that the increase in acidity is due to the presence of sulfonic anchored groups.

3.2 Catalytic studies

3.2.1 Alcoholysis of epoxides

Mesoporous carbons CMN and CMNS were tested as catalysts in the ring opening reaction of epoxides. [7]



Scheme 1 - Reaction of epoxides with alcohols. Adapted from [7]

Considering the reaction of styrene oxide and butanol at 80 °C, both catalysts are active in the ring opening reaction but the functionalized carbon with sulfonic groups, CMNS, presents higher reactivity.

The reaction in the presence of catalysts CMN presented a 99 % conversion and 83 % selectivity for the product of interest (**b**) at 180 min of reaction time, while in the presence of CMNS it was possible to obtain the same values of conversion and selectivity in only 15 min.

These results suggest that strong acid sites in CMNS, sulfonic acid groups, are more active in this type of reactions. Table 3 presents the catalytic performance of catalyst CMNS with different epoxides, showing that the structure of the reactive has great influence.

3.2.2 Methoxylation of α -pinene

CMN and CMNS were employed in the reaction of methoxylation of α -pinene with success. [5]

Again both catalysts were active in the reaction studied. In this work CMN even outperformed the commercial carbon Norit also oxidized with HNO_3 , revealing the textural relevance in the catalytic behavior of the samples. On the other hand CMNS presented higher initial reaction rate and higher conversion than CMN reinforcing the extreme importance of functional surface groups.

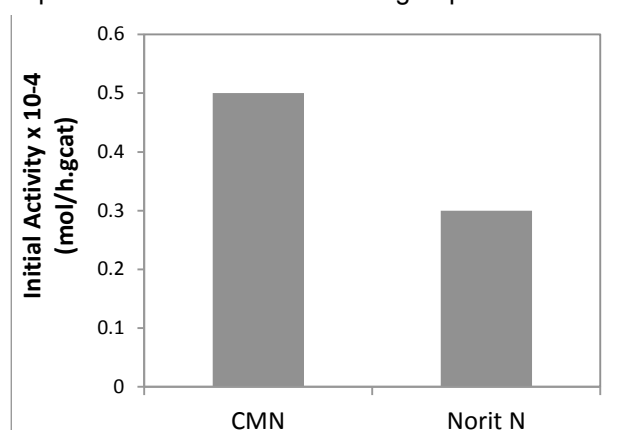


Fig 1. Methoxylation of α -pinene over activated carbon catalysts. Initial activities taken as the maximum observed reaction rate, calculated from the maximum slope of the α -pinene kinetic curve. Reaction conditions: $T=60^\circ\text{C}$; $m_{\text{cat}}=0.2\text{g}$; $n_{\alpha\text{-pinene}}=9\text{mmol}$; 50ml of methanol. Adapted from [5]

3.2.3 Synthesis of substituted quinolines

Another very interesting reaction to be studied under catalytic conditions applying carbons is the Friedlander reaction.

This is a very appealing area of research that may have great impact in the synthesis of important building blocks useful for the preparation of synthetic compounds with application in medicine, food, catalysis, dye, materials, refineries, and electronics. [16-17]

An example is the synthesis of substitute quinolones, an important class of nitrogen heterocycles. [6]

This work has been done by the research group in UNED with Doctor Elena Perez- Mayoral, presenting very promising results [6].

Among other activated carbons, the mesoporous carbon, also revealed to be able to catalyze the reactions. Its performance was less effective than the other commercial ones studied, but this may be due to a lower amount of sulfonic groups incorporated in the surface.

Conclusion

These three works were chosen to illustrate one of our group research lines, the study of catalytic behaviour of carbons.

The results summarised here exemplify that mesoporous carbon can be an effective catalyst in reactions of interest for the production of fine chemicals in the scope of green chemistry.

Mesoporous activated carbon proved to be effective catalysts for the ring opening reaction of epoxides affording the corresponding β -substituted alcohols with high conversion values and very good selectivity.

Also the HNO_3 oxidized carbon material and carbon material with sulfonic group were successfully used as acid catalysts in the methoxylation of α -pinene yielding α -terpinyl methyl ether as main product of the reaction.

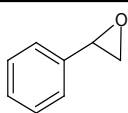

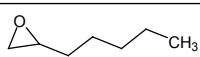
In a more complex reaction, as is the Friedlander, it presents lower performance but it is still capable of catalytic activity.

The textural properties of these materials, as well as the surface chemistry seems to be with great relevance for its performance. It is important to reinforce that the application of the catalysts reported here simplifies the experimental procedure, and allows the use of milder conditions.

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Table 3 - Ring opening of substituted epoxide with ethanol. Adapted from [7].

| Epoxide | Alcohol | T [°C] | Time [min] | Conversion [%] | Selectivity to b [%] |
|---|---------|-----------|---------------|-------------------|--------------------------------|
|  | EtOH | r.t. | 30 | 99 | 97 |
| | | 50 | 15 | 99 | 96 |
| | | 80 | 5 | 99 | 94 |
|  | EtOH | r.t. | 120 | 89 | 100 |
| | | 80 | 30 | 99 | 100 |
|  | EtOH | r.t. | 24h | 38 | 57 |
| | | 80 | 4h | 97 | 52 |

Conditions: Catalyst CMNS 0.1g, 3ml of alcohol, 1.5 mmol of epoxide.

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