



## Preparation of activated carbon-metal oxide hybrid catalysts: textural characterization



A. Barroso-Bogeat, M. Alexandre-Franco, C. Fernández-González, V. Gómez-Serrano\*

Department of Organic and Inorganic Chemistry, Faculty of Sciences, University of Extremadura, Avda. de Elvas s/n, E-06006 Badajoz, Spain

### ARTICLE INFO

#### Article history:

Received 20 February 2014

Received in revised form 10 April 2014

Accepted 17 April 2014

Available online 10 May 2014

#### Keywords:

Activated carbon

Metal oxides

Hybrid catalysts

Textural characterization

### ABSTRACT

In catalysis processes, activated carbon (AC) and metal oxides (MOs) are used as catalysts and catalyst supports because of their textural and chemical properties. A combination of AC and MO properties in a single catalyst entails changes in the catalytic activity and behaviour which would redound to the number of applications. The present study aims at preparing AC-MO hybrid catalysts by chemical interaction of MO precursors in aqueous medium with AC and at carrying out the textural characterization of the samples. From a commercial AC and six MO precursors (i.e.  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{SnCl}_2$ ,  $\text{TiO}_2$ , and  $\text{WO}_4^{2-}$ ), three series of hybrid catalysts were prepared by wet impregnation and oven-drying at 120 °C and subsequent heat treatment of the resulting products at 200 or 850 °C in inert atmosphere. The samples were characterized texturally by  $\text{N}_2$  adsorption at  $-196$  °C, mercury porosimetry, and density measurements. Therefore, the influence of the MO precursor and heating conditions on the porous texture is studied. Yield varies more widely for the samples prepared at 120 °C and 850 °C than at 200 °C. The mass increase after oven-drying at 120 °C and the mass decrease after heating at 850 °C are much greater for the Sn catalysts. Because of the support of MO precursors on AC, in general, macro-, meso-, and microporosity significantly decrease. The effects on the texture of AC are by far more important for the Sn catalyst and also, though less, for the Fe catalyst. However, they are weaker for the W and Ti catalysts. In general, the heat treatment at 200 °C only causes small changes in the porous texture of the samples. By heating at 850 °C the pore size distribution becomes more uniform in the three porosity regions. Microporosity develops chiefly for the Sn catalyst, whereas mesoporosity does mainly for the Sn and Fe catalysts. The textural modifications have been associated with mass, composition, and structural modifications.

© 2014 Elsevier B.V. All rights reserved.

### 1. Introduction

Activated carbon (AC) is used as a catalyst on its own and much more frequently as a support for catalysts [1–6]. ACs are used as catalyst supports because, as unique virtues, they gather the possibility to tailor the physical surface properties and to modify the chemical surface properties and the nature of the interaction with the catalyst, and others [2,5]. Metal oxides (MOs) represent one of the most important and widely employed categories of solid catalysts. As AC, they may also be used either as the active phase or as the support. Among the MO catalysts, those of transition metals occupy a predominant place owing to their low-production cost, easy regeneration, and selective action. MOs are utilized both for their acid–base and red-ox properties [7–9]. In the last decade, however, there has been a growing interest in the synthesis and applications of mixed MOs [10,11]. From carbon molecular sieves, composite catalysts constituted by inorganic oxides dispersed in a carbon matrix have also been prepared [12]. AC-supported metal oxide catalysts have been used

for a great variety of chemical reactions, i.e.  $\text{Fe}_2\text{O}_3$ , ZnO and  $\text{TiO}_2$ , degradation of organic compounds [13–20];  $\text{Fe}_2\text{O}_3$ , hydroxylation of benzene [21, 22], dehydrogenation of propane [23], acylation of alcohols and amines [24], and so forth;  $\text{WO}_3$ , decomposition of isopropanol [25,26], isomerization of 1-butene [27], decomposition of methanol and ethanol [28], combustion of toluene [29], hydrogenation of ethylene [30];  $\text{SnO}_2$ , low temperature oxidation of CO [31,32], AC-covered  $\text{Al}_2\text{O}_3$ , hydroprocessing and hydrodesulfurization processes [33,34].

The use of AC as support for catalysts is mainly based on its porous structure and surface functional groups. The porous structure controls the availability of surface active sites and thereby the degree of catalyst dispersion. In catalysis processes, the dispersion of the catalyst plays a key role as it enhances its efficiency. To achieve a high degree of catalyst dispersion, ACs are often used because of their high surface area. Another important factor in such processes is the pore size distribution of AC. ACs are characterized by a very broad pore size distribution ranging from molecular dimension to several hundred nanometers. Depending on the size of the reactant and of the product molecules, the catalyst dispersed in small pores would be more or less effective. Therefore, the pore size distribution is an important consideration when selecting the appropriate carbon to use as a support [35], minimizing diffusion

\* Corresponding author. Tel.: +34 924 289421; fax: +34 924 271449.  
E-mail address: [vgomez@unex.es](mailto:vgomez@unex.es) (V. Gómez-Serrano).

limitations and catalyst deactivation [36]. Typical ACs are essentially microporous materials and therefore may be texturally sensitive to the support of catalysts on their surface. On the other hand, textural properties such as surface area and porosity have a remarkable impact not only on the catalyst dispersion but also on the reduction of metal chemical species on the surface of AC, especially when the conventional incipient wetness impregnation technique is used in the preparation of the catalysts ([37] and references therein). The surface functional groups, especially oxygen complexes, present on the carbon support can provide anchorage sites for the catalyst precursor and act as active centres in multifunctional catalysts due to their acid–base or red–ox properties [38, 39]. In addition to act as nucleation anchors, it has also been reported that the surface groups can improve the access of metal solutions because of the decrease in the hydrophobicity of the carbon [37].

In view of the numerous reactions catalyzed by AC–MO catalysts and of the essential role played by the porous structure not only in the preparation of these hybrid catalysts but also in their subsequent use in catalysis processes, the focus of the present study was on the preparation and textural characterization of AC–MO hybrid catalysts. In these catalysts, it can be regarded AC as a MO support which may further behave at the same time as an active catalyst. Of course, the hybrid catalysts are susceptible to be used in the same catalysis reactions (i.e. with reactant in gas or liquid phase; red–ox, acid–base, etc.) as AC and MOs separately, being then possible to diversify the applications of such catalysts as compared to their AC and MO parents. The catalytic activity for the hybrid catalysts will be determined not only by the specific activities of AC and MOs but also by their contents in the samples. In best a synergistic effect may occur for the hybrid catalysts.

Using a commercial AC and the wide series of MO precursors, AC–MO hybrid catalysts are prepared and characterized texturally. Since catalysis processes of industrial interest need to heat at relatively high temperatures [4], at which physico–chemical properties of the catalyst may undergo modifications and thereby influence the catalytic behaviour, three series of hybrid catalysts are prepared by heating under different conditions. The resulting samples are characterized in terms of porous structure by gas adsorption at low temperature, mercury porosimetry, and density measurements.

## 2. Experimental

### 2.1. Materials and reagents

A granular AC from Merck® (Darmstadt, Germany), 1.5 mm average particle size (Cod. 1.02514.1000), as received, was used as MO support. For AC, the ash content is 4.72 wt.%, which is markedly lower than for other activated carbons that may contain up to 15 wt.% of mineral matter (the nature and amount are a function of the precursor) [4]. Ashes are composed of mullite and SiO<sub>2</sub>. The elemental composition (wt.%) is: C, 86.5; H, 0.51; N, 0.26; S, 0.64; O, 7.37. pH of the point of zero charge is 10.50. Metal nitrates, which are readily soluble in water, as a rule were used as MO precursors. These were Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, SnCl<sub>2</sub>·2H<sub>2</sub>O, Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, all of them purchased from Panreac® (Barcelona, Spain) and being of reagent grade. As an exception to the rule, anatase powder (Aldrich®; Steinheim, Germany) was used as TiO<sub>2</sub> precursor.

### 2.2. Preparation of hybrid catalysts

Most hybrid catalysts were prepared by the well-known method of wet impregnation [40]. Around 25 g of AC were impregnated with 250 mL of an aqueous solution of the corresponding MO precursor, using a precursor to AC ratio of 1:1. The impregnation system was placed in a three necked flask and heated at 80 °C under continuous mechanical agitation of 100 rpm for 5 h. Once this time had elapsed, the impregnated products were first vacuum-filtered with aid of a water pump and then oven-dried at 120 °C for 24 h.

The AC–TiO<sub>2</sub> hybrid catalyst was prepared by slightly modifying the method of impregnation at high temperature previously proposed by Kahn [41,42]. In such a method, 25 g of AC were impregnated with 250 mL of an aqueous suspension containing 1.25 g of anatase powder, by heating also at 80 °C for 5 h under continuous stirring of 300 rpm. Then, after vacuum–filtration, the resulting solid in two successive steps was thoroughly washed with deionised water until total colour loss in the residual liquid and oven-dried at 120 °C for 24 h. Anatase was selected as the catalyst precursor because the photocatalytic activity of TiO<sub>2</sub> seems to be mainly associated with the anatase-type structure [43].

Subsequently, the oven-dried products were calcined at 200 or 850 °C in a horizontal cylindrical furnace. About 2 g of product were weighed in an analytical balance, placed in a small steel container, and heated from room temperature up to the calcination temperature in an inert atmosphere of high purity (i.e. >99.998 vol.%) nitrogen (flow rate = 100 mL·min<sup>−1</sup>). The heating rate was 10 °C·min<sup>−1</sup>. The holding time at maximum heat treatment temperature was 2 h. Next, the system was allowed to cool down to room temperature under the same flow of nitrogen. These experiments were carried out in duplicate or in triplicate in order to obtain the required mass of each catalyst for later studies. For comparison purposes, two samples were obtained by heating only AC, in the absence of any metal oxide, under the same conditions as in the preparation of the hybrid catalysts.

The yield of the process of preparation of the catalyst samples was calculated as (M<sub>f</sub>/M<sub>i</sub>) × 100, with M<sub>i</sub> being the mass either of AC (i.e. 25 g) used in the impregnation treatment or of the samples of series 1 used in the subsequent heat treatment, whereas M<sub>f</sub> is the mass of final product after oven-drying at 120 °C or heat-treating at 200 or 850 °C. As a whole, three series of catalyst samples were prepared, i.e. three of these samples with each MO, depending on heating conditions in the oven-drying and calcination treatments. They are: series 1: 120 °C, 24 h; series 2: 200 °C, 2 h; series 3: 850 °C, 2 h. The codes assigned to the catalysts are shown in Table 1. The samples prepared from AC are referred to in the text as AC200 and AC850.

### 2.3. Textural characterization study

The textural characterization of the samples was accomplished by gas adsorption (N<sub>2</sub> at −196 °C), mercury porosimetry, and helium and mercury density measurements. The N<sub>2</sub> adsorption isotherms were determined using a semiautomatic adsorption apparatus (Autosorb 1), Quantachrome®. About 0.10 g of sample was first oven-dried at 110 °C overnight and then out-gassed at 120 °C for 12 h, at a pressure lower than 10<sup>−3</sup> Torr, prior to starting adsorption measurements under equilibrium conditions. The out-gassing temperature was selected in accord with the temperature of preparation of the catalyst samples of series 1. The N<sub>2</sub> isotherm provides valuable information on the pore size distribution in the regions of micro- and mesopores (i.e. macropores are not amenable to the gas-adsorption analysis), surface area, and pore volumes. In relation to the various porosity regions it is relevant to point out that a widely accepted classification of the pores by their average width (w) is: micropores, w < ~20 Å; mesopores, ~20 Å < w < ~500 Å, and macropores (w > ~500 Å) [44]. The pore size distribution in the

**Table 1**  
Preparation of the metal oxide–AC catalysts. Sample codes.

| Precursor  | Heat treatment temperature |        |        |
|--|----------------------------|--------|--------|
|  | 120 °C                     | 200 °C | 850 °C |
| Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O | A120                       | A200   | A850   |
| Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O | F120                       | F200   | F850   |
| SnCl <sub>2</sub> ·2H <sub>2</sub> O                 | S120                       | S200   | S850   |
| TiO <sub>2</sub> anatase                             | T120                       | T200   | T850   |
| Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O   | W120                       | W200   | W850   |
| Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O | Z120                       | Z200   | Z850   |

Download English Version:

<https://daneshyari.com/en/article/209705>

Download Persian Version:

<https://daneshyari.com/article/209705>

[Daneshyari.com](https://daneshyari.com)