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Influence of surfactants on the physicochemical properties and catalytic behaviour of Mo-doped carbon xerogels

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ABSTRACT

A series of Mo-doped carbon xerogels were obtained by surfactant-assisted sol-gel polymerization of resorcinol-formaldehyde at neutral pH. The morphology, porous texture, acid-base character and metal phase and dispersion, of these novel nanostructured materials were studied by several and complementary techniques, while their catalytic performance was assessed in the isopropanol decomposition and *n*-hexane aromatization. The formation of different carbon nanostructures (nanospheres or nanofibers) was induced by fitting the surfactant ratios, being always obtained highly dispersed molybdenum nanoparticles on these nanostructures. Nevertheless, the nature of the Mo-phases varied from oxides to carbides depending on surfactant ratios. The incorporation of cationic surfactant molecules to the chemical structure of the gels favours the interaction with anionic precursors, like MoO_4^{2-}, which avoids sintering and promotes the carbidization of the metallic phase (63% of the total metal loading being achieved) during carbonization. The combination of Mo-phases (oxide and carbide) together the carbon support moderates the catalyst acidity, which induces a high selectivity to benzene (around 75%) in hexane aromatization processes.

1. Introduction

Carbon gels are a new type of carbon materials with outstanding properties to be applied in catalysis [1,2]. Since original Pekala's method [3,4], multiple variations have been proposed to fit their morphology, porous texture and chemical composition for specific applications. This fact is based on the flexibility of the sol-gel method that allows combining and modifying many different parameters during the preparation of the initial solutions (e.g., nature of monomers [5,6], solvents [7,8], reactant ratios [9], polymerization catalysts [10,11] and pH [12]), experimental conditions of polymerization or curing steps [13], drying method (aerogels, xerogels or cryogels can be obtained) [14] and finally, carbonization and/or activation processes [15,16].

Thus, a large amount of variables should be carefully controlled, each combination leading to samples with very different physical characteristics, morphologies, shapes and dimensions [17]. In general, supercritical drying preserves in a large degree the porous structure of the hydrogel, avoiding the collapse of porosity by shrinkage and resulting in carbon aerogels with a more developed porosity than their corresponding xerogels obtained by subcritical drying [5]. Nevertheless, the application of supercritical drying method at large scale makes the preparation of aerogels difficult and expensive. Cryogels are cheaper materials, prepared by the freeze technology often used in the industry. However, this kind of materials presents problems in the structure of the pellets, such as the apparition of cracks and defects [18], which decrease the mechanical resistance. Therefore, the production of xerogels, which possess *a priori* a lower porosity than cryogels and aerogels, progressively becomes an interesting alternative favoured by the employ of available, quick and economic drying techniques (e.g., microwave) [1,19]. In addition, the xerogel properties can be fitted by adjusting the preparation recipe [20,21], or minimizing the shrinkage with a previous exchange of water by other solvents with higher vapour pressure, like acetone [19].

On the other hand, the use of surfactants in the polymerization media strongly determines the morphology, shape, dimensions and crosslinking of the primary particles [22–25], thus the porosity and mechanical strength of carbon aerogels or xerogels being determined. Based on the ability to fit both physical and chemical properties, carbon gels demonstrated high performances when used as catalysts or catalyst supports in different processes.

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Looking to improve their catalytic application, the preparation of metal-doped carbon aerogels by solving the metal salt precursors into the starting organic solutions was firstly proposed in 1999 [15]. In this context, metals are present along all the synthesis process, their ability to catalyse the steps of polymerization, carbonization and activation being also demonstrated [16,26–28]. In fact, the morphology, porous characteristics and chemical nature of organic aerogels are strongly influenced by the metal used during polymerization [15,16]. Chemical and structural transformations in both organic and inorganic phases also occur simultaneously during the carbonization. Thus, the graphitization of amorphous polymeric organic gels [26] and the reduction of the metal precursor by the organic matrix with formation of intermediate oxides, or even carbides, were previously observed [26–28], these processes being widely affected by the metal nature and experimental conditions used. Alternatively, metal-doped carbon gels were also synthetized by ion-exchange on the hydrogel [29,30], and obviously, supported catalysts can be prepared by impregnation of a carbon gel support previously obtained [31,32].

The surfactant nature (anionic, cationic or non-ionic) markedly influenced on the characteristics of Mo-doped carbon xerogels and the electrostatic interactions between metal and carbon phases, which in turn determined the metal loading and sintering [33,34]. In the current study, the synthesis of metal-doped carbon gels was further modified by using co-surfactants in different ratios. The influence on the nanostructures of both carbon supports and Mo-phases was studied, as well as the dispersion, acid-base character, nature and ratio of the active phase formed. Finally, the catalytic properties of the resulting materials were evaluated by isopropanol decomposition and *n*-hexane aromatization.

2. Experimental

2.1. Sample preparation

Organic xerogels were prepared by the sol-gel polymerization of resorcinol (R) and formaldehyde (F) using water (W) as solvent, and different portions of hexadecyl trimethylammonium bromide (CTAB), *tert*-butanol (*t*-BuOH) and/or 1,3,5-trimethyl benzene (TMB) as surfactants (S), according to recipes summarized in Table 1. In all cases, the R/F molar ratio and the reactant concentration (R/W) were constants. A xerogel was prepared without any S as reference material (X sample). In the other samples, the cationic CTAB surfactant (S) was always used to favour the attractive molybdate – RFS interactions [33,34], while R/*t*-BuOH and R/TMB molar ratios varied. The sample nomenclature indicates the surfactants present.

In a typical synthesis procedure, a starting aqueous solution containing R and the corresponding surfactants was prepared and the pH fitted to values around 7.5. The resulting RS solution was heated in an oil bath to 50 °C under vigorous stirring and reflux and then, formaldehyde (F) was added drop-wise for polymerization. The suspension formed was aged for 2 h at 50 °C to guarantee the complete gelation. Then, Mo-doping was carried out by dropping the appropriate amount of $(NH_4)_6Mo_7O_{26}\cdot 4H_2O$ previously dissolved in the minimum amount of water to reach a Mo loading of 1 wt.% (regarding R-F reactants), afterward the temperature was increased until 90 °C, these conditions being kept for additional 24 h to complete the polymer curing. Further, the suspension was cooled down at room temperature and the solid product filtered and washed with water and ethanol, to remove un-reacted reagents. Finally, the wet product was dried at atmospheric pressure, first 12 h at 50 °C and finally 12 h at 120 °C. The organic Mo-doped xerogels were thereafter carbonized in a nitrogen flow (100 cm^3/min) in a tubular furnace, using a heating rate of 2 °C/min up to 900 °C and a soak time of 5 h.

Table 1
Nomenclature and concentration of reactants (in molar ratio) used in the corresponding recipe.

Sample	R/F	R/W	R/CTAB	R/TMB	R/*t*-BuOH
X	1/2	1/180	–	–	–
XS	1/2	1/180	2/1	–	–
XS-Bu	1/2	1/180	2/1	–	1/1
XS-T	1/2	1/180	2/1	2/1	–
XS-TBu	1/2	1/180	2/1	2/1	1/1

2.2. Sample characterization

The chemical nature of the organic xerogels was determined by FTIR spectroscopy and thermogravimetric analysis (TG-DTG). The IR absorption spectra were recorded on a Nicolet 20SXB FTIR spectrometer using KBr pellets. The pyrolysis process was simulated and studied by TG experiments, performed with a heating rate of 10 °C/min under 60 cm^3/min N_2 flow using a thermobalance model TGA-50H.

The textural and chemical characterization of the carbon xerogels and Mo-supported carbon xerogels were also performed by various techniques. The chemical nature and dispersion of the Mo-phase were analyzed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM). XRD measurements were carried out using a Bruker D8 Advance diffractometer and the corresponding XRD-patterns analyzed on the basis of JCPDS files. The morphology of the doped-carbons was observed by scanning electron microscopy (SEM) with a Leo (Carl Zeiss) Gemini-1530 microscopy, while the particle dispersion analysis was studied by HRTEM images acquired with a Phillips CM-20 electron microscope.

XPS measurements were made by an Escalab 200R system (VG Scientific Co.) equipped with MgKα X-ray source ($h\nu = 1253.6$ eV) and hemispherical electron analyzer. For these measurements, the binding energy (BE) values were referred to the C_{1s} peak at 284.6 eV. Prior to the analysis, the xerogels were evacuated at high vacuum and then introduced into the analysis chamber. A base pressure of 10^{-9} mbar was maintained during data acquisition. Survey and multi-region spectra were recorded at C_{1s}, O_{1s} and Mo_{3d} photoelectron peaks. Each spectral region of photoelectron interest was scanned several times to obtain good signal-to-noise ratios. The spectra obtained after background signal correction were fitted to Lorentzian and Gaussian curves in order to obtain the number of components, position of the peak and peak areas, as well as the surface abundances taking into account the sensitivity factors reported elsewhere [35].

The textural properties of carbon xerogels were determined by physical adsorption of N_2 (−196 °C) and CO_2 (0 °C) using Autosorb-1 Quantachrome. The BET surface area was obtained by applying the BET equation to the N_2-adsorption isotherms. Information more detailed on the micropore volume (W_0) and the characteristic adsorption energy (E_0) were determined by the application of the Dubinin-Radushkevich (DR) equation to both CO_2- and N_2-adsorption isotherms, while the mean micropore width (L_0) and the micropore surface area (S_{mic}) were calculated by applying the Stoeckli equations as previously described [36].

2.3. Catalytic tests

Since the metal precursor salts were decomposed during the carbonization process, an additional pretreatment of the material was not necessary. The decomposition of isopropanol was used to evaluate the surface acidity as a model reaction. Catalytic tests were carried out in a quartz microreactor at atmospheric pressure with

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