Thesis Review. Selective hydrogenation of α,β-unsaturated aldehydes and photodegradation of pollutants using catalysts based on carbon xerogels

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OBJECTIVES AND NOVELTY

The overall research objective of this study was the development of new synthesis methods of advanced materials based on carbon xerogels including structured pure carbon xerogels with controlled porosity and morfology as well as composites materials based on carbon xerogels-inorganic oxides and carbon xerogels-carbon nanofibers composites, in order to obtain suitable materials for very different applications: a) selective hydrogenation of α,β-unsaturated aldehydes, b) photocatalytic degradation of pollutants and c) biomedical applications. For the use of these materials in both catalytic applications, special attention is given to the optimization of parameters such as its microstructure, porosity, acidity, dispersion and metal-support interactions, type of active centers, etc. Thus, the synthesis methods previously developed in our laboratories have been adapted to optimize the properties of these materials to each of the proposed applications. These properties were also finally modified by different functionalization reactions to be used in medical applications. In this case, special attention to aspects like toxicity, biocompatibility, etc, were considered.

RESULTS

The selective hydrogenation of α,β-unsaturated aldehydes requires specific catalysts that favor the hydrogenation of the C = O group instead of the C = C one, more favorable kinetic and thermodynamically [1]. In the development of specific catalysts for such reaction, the influence of the support (inorganic supports, activated carbons, carbon xerogels and composites), the active phase (Pt, Ir or Ru) and the pre-treatment conditions (P_{H2}, T, agitation, contact time) have been studied. Intensive physical and chemical characterization of the supports and catalysts using a variety of complementary experimental techniques is performed. The reaction conditions and metal particle size is also optimized to ensure the absence of diffusional limitations and maximum performance. Thus it has been possible to establish correlations between the physicochemical properties of the supports and catalysts with its catalytic performance, more specifically, the yield to unsaturated alcohols (UA). The influence of the chemical and porous characteristics of both carbon and inorganic supports used to develop Pt-catalysts is studied. Using carbon supports (activated carbons and carbon xerogels), the performance of the derivatives Pt-catalysts strongly depends on the micro/mesoporous character of the supports and the presence of impurities, namely inorganics components. Mesoporosity and acid impurities leads to a decrease of UA yields, thus best results were obtained with microporous carbon xerogels (Figure 1) [2,3]. Similar conclusions were obtained when using inorganic supports, mesoporosity favors secondary reactions (consecutive hydrogenations, cyclization, etc) inside the pores, while mainly Brönsted acidity strongly favour cracking reactions [3]. In such a basis, Al_2O_3 always provides worse results than TiO_2 as Pt-supported catalysts for citral hydrogenation, in spite of their similar porous and pH_{pzc} values, while the microporous carbon xerogel structured in microspheres provides the highest selectivity to unsaturated alcohol, even higher than other bibliographic results for monometallic catalyts.

This behavior also depends deeply on the pretreatment conditions of the catalyst, which determine the chemical and crystalline transformation as well as the active phase dispersion. In spite that Pt-sintering in general is favored by H_2-pretreatment regarding the He-ones [3], which should lead to a stronger catalyst deactivation, in the case of Pt/TiO_2 catalysts the catalytic performance is improved after the H_2-pretreatment (Figure 2). This is because the H_2 treatment favors simultaneously the partial reduction of the TiO_2 surface, in such a way that the combination Pt site/oxygen vacancy has been identified as the real selective catalytic site to UA during citral hydrogenation [4].

Another important factor to take into acount is the active phase and the particle size because this type of hydrogenation reactions is structure sensitives.

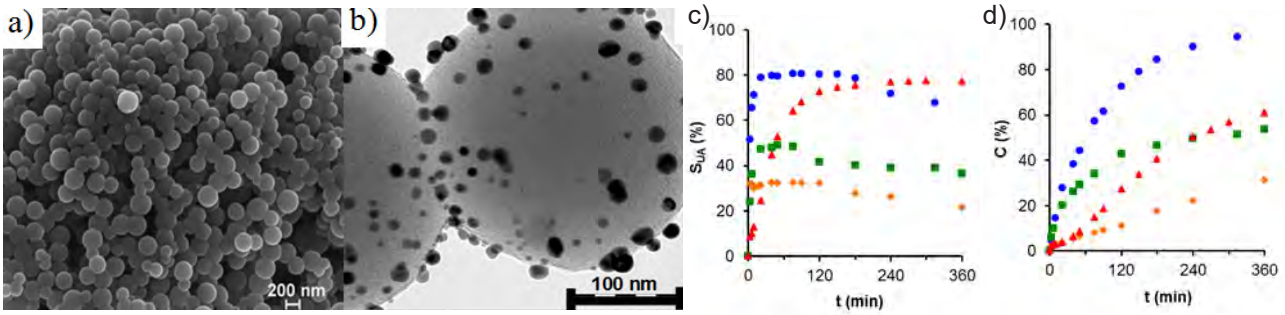

Figure 1. a) SEM images of carbon xerogel structured in microspheres and b) its corresponding Pt supported catalysts. c) Selectivity to unsaturated alcohols and d) conversion using Pt catalysts sopported on: TiO_2 (●), carbon xerogel A8 (▲), Al_2O_3 (■) and SiO_2 (◆).

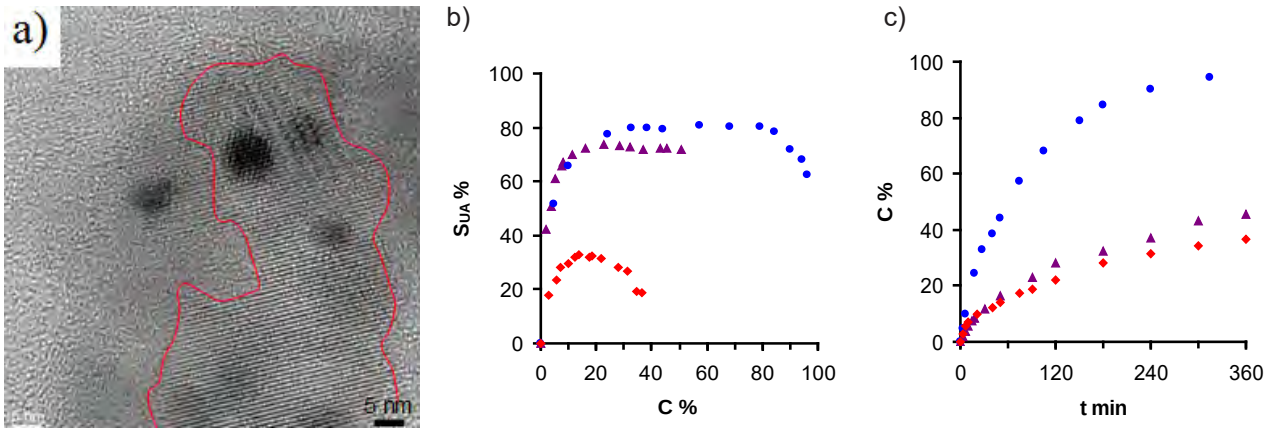

Figure 2. a) HRTEM images of Pt/TiO_2-H_2, b) selectivity to unsaturated alcohols and conversion after different treatment atmosphere of Pt/TiO_2: He (◆), H_2 (●) and He,H_2 (▲)

The metal particle size was optimized, for that; Pt-catalyst was pretreated under different experimental conditions obtaining Pt particles size from 2 to 10 nm. After test in the selective hydrogenation of citral it was pointed out that the optimum particle size is around 8 nm. Regarding the metal phase, a series of monometallic Pt, Ir and Ru-catalysts deposited on carbon xerogel microspheres was prepared, exhaustively characterized and used in the selective hydrogenation of citral. A similar metal particle size is obtained in all cases after He-pretreatment, allowing the comparison between metals; the catalytic activity increases in the sense Ir < Ru < Pt [5]. Sintering is favoured when catalysts are pretreated in H_2-flow leading to an important loss of activity, especially for Ru-catalysts. Pt and Ir-catalysts are more selective than Ru-catalysts, reaching selectivity values to unsaturated alcohols of around 80%. Thus, in terms of yields to these valuable products Pt-catalysts seem to be the most appropriate active phase. Nevertheless, reutilization experiments showed that Ir-catalyst maintained the catalytic performance while a severe deactivation is observed for Pt-catalysts. Deactivation was related with the chemisorption of CO or CO-evolving molecules on the Pt-surface.

These results open new opportunities in the preparation of highly selective hydrogenation catalysts combining the ability of TiO_2 to produces specific active site for citral adsorption through the C = O bond and the developed porosity and fitted surface chemistry (basicity) of carbon materials. The sol-gel synthesis procedure guarantees the purity of these supports avoiding interferences of the mineral matter present on classical ACs. The high surface areas of carbon xerogels facilitate the dispersion of the titanium dioxide particles and their reduction so, maximizing the strong metal-support interactions (SMSI effect) and Pt-dispersion.

So that, new carbon xerogels-inorganic oxide (ZrO_2, TiO_2, SiO_2, V_2O_5 and CeO_2) composites were prepared and used as Pt-support to develop catalysts for the selective hidrogenation of citral, obtaining specific and high active catalysts for the selective C=O hydrogenation of α,β-unsaturated aldehydes (more than 95 % of S_{UA} at total conversion). The synthesis method of these composites comprises resorcinol and formaldehyde polimerization in an organic medium simultaneously with the hydrolisis of a metal alkoxide precursor of the inorganic oxide. This method, was recently patented [6-8], and consists in an orderly and efficient sequence of specific steps that determine the final catalytic properties of these materials, for example the use of surfactant compounds, strict control of the polymerization temperature and stirring speed, a very slow addition of reactants or the use of microwave for the drying step. Under these conditions a very high dispersion of the metal oxide in the carbon xerogel matrix is achieved, maximizing the metal-support interactions in the resulting supported catalysts, which allows to obtain very high activities and selectivities at relatively mild reaction conditions, avoiding the use of supercritical solvents or bimetallic catalysts.

Given the nature of TiO_2/C composite materials, the study of their applications in photo-catalysis, specifically degradation processes of typical water pollutants such as azo dyes are further raised. The objective here was to optimize the material for enhanced its performance under visible radiation, but also carried out experiments using ultraviolet radiation. Alternatively, TiO_2 coating carbon xerogel spheres are also prepared (Figure 3). This TiO_2 coating is stable enough for use in the catalytic conditions tested. The crucial step is the pre-gelation of resorcinol-formaldehyde and the formation of nanostructures prior to coating. These new materials have been tested in the photo-degradation of Orange G using visible light obtained very good results. Results were compared in basis of decolourization, TOC analysis to determine the formation of oxidation intermediates and toxicity of the corresponding solutions using a standard method with luminescent bacteria (Vibrio Fisheri, NRRL-B-11177, in accordance with the European guideline ISO 11348-2:2007). The hydrophobic/hydrophilic nature of this material allows its precipitation in aqueous solution after completion of the decontamination process, which enables an easy separation of the photocatalyst after the reaction, with the advantage that this means in real applications.

Considering the progressive advance of the use of carbon materials in biomedical applications, and given that no references of the use of these materials in such applications have not been found despite the excellent properties of carbon aerogels and xerogels, a new line is also opted for studied during a stay at the University of Trieste, under the supervision of Prof. Maurizio Prato, one of the great specialists in these issues. For this, different carbon-based xerogel composites (gel materials and carbon gel-carbon

nanofibers, Figure 4a) were functionalized through reactions known as Tour and Prato (addition of aryldiazonium salts generated in situ and 1,3-dipolar cycloaddition of azomethine ylides, respectively) reaching high levels of functionalization compared with other materials commonly used in this field. Results of toxicity studies of such samples, evaluated in the presence of osteocytes, show the null toxicity of the samples . In addition, samples were not only non-toxic but also a cell growth was also observed increasing the concentration of carbon material in the culture medium, indicating a beneficial effect of the carbon material in the cell growth (Figure 4b). Therefore, this study points out that carbon xerogels could be interesting materials for biological applications, showing no toxicity due to their high purity and allowing high degrees of functionalization, which opens a new and very interesting field for the application of these carbonaceous materials.

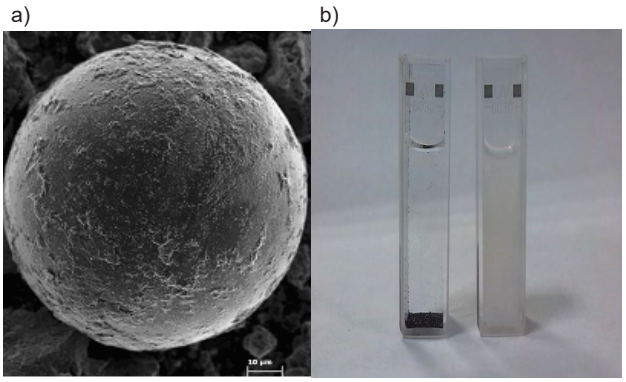

Figure 3.- a) SEM images of carbon xerogel microspheres coated with TiO_2 and b) suspensions of the photo-catalysts after reaction. Left (carbon xerogel microspheres coated with TiO_2); right (P25).

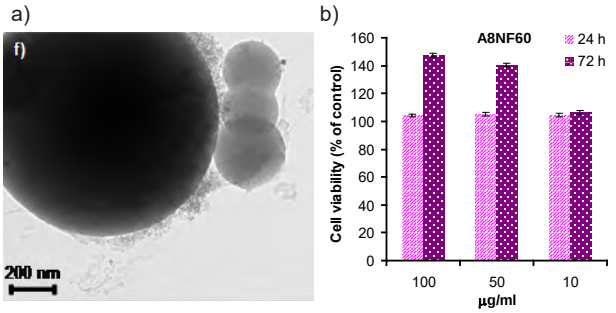

Figure 4.- a) TEM microphotograph of carbon gel-carbon nanofibers composite and b) LDH assay after incubation with carbon materials in fibroblast cell line at different carbon concentration for indicated times.

CONCLUSIONS

Different series of materials, including pure carbon xerogels and carbon – inorganic oxides composites were synthesized and deeply characterized. Their characteristics were fitted to a determined application. Catalysts to be used in the selective hydrogenation of citral and photocatalysts for the degradation of pollutant in water solutions were developed. Some samples were also applied for medical applications.

Hydrogenation catalysts were prepared by impregnation of the corresponding carbon-based supports with transition metals (Pt, Ir, Ru). Experimental parameters (T, PH_2, stirring, etc) were previously optimized and then, the physicochemical characteristics of catalysts were also fitted in order to obtain a high yield of unsaturated alcohols. The combination of carbon xerogels with TiO_2 provides a synergetic effect when used as Pt-support enhancing the S_{UA} up to 90%.

These materials also present very high photocatalytic activity for the degradation of pollutants in water. Again, a synergetic effect between both phases avoiding recombination of electrons, lowering the band-gap of the photocatalyst and favouring the adsorption of pollutants by increasing the porosity and surface area, permit a high performance and the use of visible radiation.

Finally, some of these materials were functionalized through reactions known as Tour and Prato. Results of toxicity studies, evaluated in the presence of osteocytes, show the null toxicity of the samples. Osteocites growth is favoured by increasing the carbon concentration. These samples can be used therefore also for the development of biological tissues.

RELATED PUBLICATIONS

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