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Glycerol oxidation with gold supported on carbon xerogels: Tuning selectivities by varying mesopore sizes

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ABSTRACT

Two carbon xerogels (CX) with different pore size distributions were prepared by the conventional approach (condensation of resorcinol and formaldehyde). The key variable to control those sizes is the pH of the aqueous solution. Gold nanoparticles were supported on the prepared CXs by the sol immobilization method and tested in the selective oxidation of glycerol, with the main purpose of evaluating the influence of the textural properties on the activity and selectivity. Mesopore sizes of the support have a strong effect on the distribution of products: wide pores enhance the formation of dihydroxyacetone whereas narrow mesopores favor the oxidation towards glyceric acid. Additionally, the selectivity results obtained with carbon xerogels were compared with those achieved with other carbon supports (activated carbon and multi-walled carbon nanotubes) and the same trend was observed. Therefore, it seems that the distribution of products can be controlled by the adequate choice of the support. For this purpose, carbon xerogel is a promising material since its pore size can be easily modified in a controllable way during the preparation stage.

1. Introduction

Over the last decade, biodiesel has emerged as a viable clean fuel. Nevertheless, its increasing global demand has created a major surplus of glycerol [1]. The valorization of this highly versatile molecule is a research area that has received tremendous attention in recent years, as glycerol is nontoxic, easily available, biodegradable and a potential starting material for numerous value-added chemicals [1,2].

Liquid phase catalytic oxidation is a promising route to convert glycerol into useful compounds, provided that the catalyst used is sufficiently active and selective for the formation of chemicals such as glyceric acid (GLYCEA) and/or dihydroxyacetone (DIHA), potentially useful as chemical intermediates in the fine chemicals industry, particularly in pharmaceuticals [1,2]. However, due to the high functionality of glycerol, a complex reaction pathway exists [2–4].

Platinum, palladium and rhodium catalysts have been described as highly active for the oxidation of glycerol in the liquid phase [5–8]. However, catalysts that are based on these metals deactivated at increasing reaction time due to oxygen poisoning [9,10]. On the other hand, gold has a better resistance to oxygen poisoning, allowing for the use of higher oxygen partial pressures [11,12]. Nano-sized gold particles supported on different carbon materials (e.g. carbon black, activated carbon and graphite) and oxides (TiO_2, MgO and Al_2O_3) are active for the oxidation of glycerol but show very different performances, carbon supported gold catalysts being more active than most oxides supported catalysts [11,13,14]. Moreover, an increasing number of studies suggest that textural and chemical properties of the support influence directly the selectivity of the process [15–18]. Recently, we reported that the use of multi-walled carbon nanotubes as support for Au nanoparticles results in the preferential oxidation of the secondary hydroxyl group and subsequent formation of DIHA; on the other hand, an activated carbon supported gold catalyst, with similar metal content and average particle size, promotes the formation of glyceric acid [18]. It was suggested that the peculiar porous characteristics of MWCNTs, including the presence of large mesopores, may favor the oxidation towards dihydroxyacetone due to a different adsorption mode. The same explanation was proposed by Prati et al. [17] when testing gold supported on carbon nanofibers for the oxidation of glycerol under base-free conditions. Therefore, it seems that the support textural properties, namely mesopore sizes, can be a key factor in order to tune the selectivity of catalysts. For this purpose, carbon xerogel (CX) is a promising material since its pore size distribution can be easily modified in a controllable way [19]. Until now, this material has not been investigated as support for gold nanoparticles in the scope of the liquid phase oxidation of glycerol. However, these polymer derived mesoporous carbon materials have been

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drawing increasing attention for catalytic applications since they possess high surface area, high porosity, high stability in acid and basic media, open pore network and controllable pore size [19]. A suitable support material is crucial for good catalytic activity and stability. Carbon materials are widely used since they present advantages as high stability in acidic and basic media. This feature is primordial in gold catalyzed glycerol oxidation since reactions are performed in a high pH medium [16,20,21]. Moreover, carbon supports offer the possibility of recovering precious metals by burning off spent catalysts. Therefore, CXs possess excellent characteristics as catalyst support.

In the present work, two mesoporous carbon xerogels having different pore sizes were prepared and used as support in the preparation of gold catalysts. Then, the prepared catalysts were evaluated in the liquid phase glycerol oxidation, in order to investigate the possible role of the mentioned property on the catalytic performance.

2. Experimental

2.1. Preparation procedures

Two carbon xerogels differing in their textural properties were synthesized. Subsequently, gold was supported on these materials by the sol immobilization method.

2.1.1. Preparation of carbon xerogels

Two carbon xerogels were prepared by the sol–gel condensation of resorcinol and formaldehyde at two different pHs (5.5 and 6.0), and subsequent carbonization of the dried gels, according to Job et al. [19].

In this procedure, 30 g of resorcinol were dissolved in 57 mL of distilled water under magnetic stirring. After dissolution the pH was about 3; then it was adjusted to a value close to the chosen one by the addition of 2 M NaOH aqueous solution. Subsequently, 40 mL of formaldehyde solution (37 wt%, containing 10–15 wt% MeOH) were added to the resorcinol solution under continuous stirring. The final pH value was then adjusted by addition of diluted sodium hydroxide solution (0.5 M). Stirring continued for 90 min, and then it was stopped, the magnetic bar was removed, and the content was left for 3 days in a shaker at 85 °C to perform the gelation. The hard gel formed was then ground and water was removed by drying in an air oven for a period of 7 days. The temperature was increased stepwise from 60 to 150 °C as following: 1st day at 60 °C, 2nd day at 80 °C, 3rd day at 100 °C, 4th day at 120 °C, and from 5th to 7th day at 150 °C. Mesoporous carbon samples were obtained by pyrolysis of the dried gels under nitrogen flow (100 cm^3 min^{-1}, STP) at 800 °C in a tubular furnace. The heating program included the following sequential steps: (1) ramp at 2 °C min^{-1} to 150 °C and hold for 60 min; (2) ramp at 2 °C min^{-1} to 400 °C and hold for 60 min; (3) ramp at 2 °C min^{-1} to 600 °C and hold for 60 min; (4) ramp at 2 °C min^{-1} to 800 °C and hold for 360 min; (5) cool slowly to room temperature. A shrinkage corresponding to approximately 50 wt% was observed after carbonization.

The carbon xerogels obtained were designated as 5CX (sol–gel processing at pH 6.0) and 20CX (sol–gel processing at pH 5.5). The numbers 5 and 20 correspond to the most frequent mesopore diameters of the samples (in nm), as it can be seen in Section 3.1.1. These materials were ground to a particle diameter between 0.1 and 0.3 mm before use, in order to avoid mass transfer resistance effects and facilitate the accessibility of reactants to gold active sites.

2.1.2. Preparation of catalysts

Catalyst samples were prepared via the sol immobilization technique, using polyvinyl alcohol (PVA) as protective agent and $NaBH_4$ as reducing agent [22]. Briefly, $HAuCl_4 \cdot 3H_2O$ (35.1 mg) was dissolved in 690 mL of H_2O, and PVA was added (1.6 mL, 0.2 wt%) under stirring. Then, $NaBH_4$ (4 mL, 0.1 M) was introduced in the yellow solution under vigorous magnetic stirring, leading to the generation of a ruby-red metallic sol. After a few minutes, the colloid was immobilized by adding the carbon xerogel under fast stirring. The amount of support was calculated in order to have a final gold loading of 1 wt% in the catalyst. When the solution became colorless, the suspension was filtered. The catalyst was washed thoroughly with distilled water until the filtrate was free of chloride (checked by the $AgNO_3$ test) and dried at 110 °C for 24 h.

The organic scaffold was removed by heat treatment under nitrogen flow for 3 h at 350 °C, and then the catalyst was activated by reduction under hydrogen flow for 3 h also at 350 °C.

This method typically provides nanoparticle sizes around 5–6 nm both in activated carbon and carbon nanotubes [12,18,22].

2.2. Characterization

Catalysts and supports were characterized by N_2 adsorption at −196 °C in a NOVA Quantachrome Instruments apparatus. BET surface area (S_{BET}), mesopore surface area (S_{meso}) and micropore volume (V_{micro}) were calculated using the BET equation and the *t*-method, respectively. Pore size distributions were obtained from the desorption branch of the isotherm using the Barrett, Joyner and Halenda (BJH) method.

The determination of oxygenated surface functional groups was performed by temperature programmed desorption–mass spectrometry (TPD–MS) [23,24]. CO and CO_2 TPD spectra were obtained with a fully automated AMI-200 equipment (Altamira Instruments). In a typical experiment, the sample (150 mg) was placed in a U-shaped quartz tube inside an electrical furnace and subjected to a 5 °C min^{-1} linear temperature increase up to 1100 °C under helium flow (25 cm^3 min^{-1}, STP). A quadrupole mass spectrometer (Dymaxion 200, Ametek) was used to monitor CO and CO_2 signals. For quantification of the CO and CO_2 released, calibration of these gases was carried out at the end of the analysis.

The gold loading of the prepared catalysts was determined in duplicate by inductively coupled plasma–optical emission spectroscopy (ICP/OES) in an external laboratory (CACTI Vigo, University of Vigo), using a PerkinElmer Optima 4300 DV spectrometer.

Electron micrographs of samples were obtained at CACTI Vigo, University of Vigo, using a JEOL 2010F instrument. Size distributions were determined by the measurement of more than 200 nanoparticles and the average diameter was calculated by $d_M = \sum d_i n_i / \sum n_i$, where n_i is the number of particles with diameter d_i.

2.3. Catalytic experiments

In standard tests, a NaOH solution and the gold catalyst (700 mg) were added to a 0.3 M aqueous solution of glycerol (total volume 195 mL; NaOH/glycerol molar ratio = 2) under stirring at 1000 rpm. The reactor was pressurized with nitrogen at 3 bar. After heating to 60 °C under this atmosphere, the reaction was initiated by switching from inert gas to oxygen (3 bar). The stirring speed of 1000 rpm was selected on the basis of preliminary experiments, which showed that external mass transfer limitations were overcome in these conditions.

The reaction was monitored by taking samples (0.5 mL) for analysis at regular time intervals. The quantitative analysis of the mixtures was carried out by high performance liquid chromatography (HPLC). The chromatograph (Elite LaChrom HITACHI) is equipped with an ultraviolet (210 nm) and a refractive index detector in series. Compounds were identified by comparison with standard samples and concentrations were calculated using calibration curves previously determined.