



Catalytic oxidation of crude glycerol using catalysts based on Au supported on carbonaceous materials

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ABSTRACT

Au catalysts supported on different carbon materials, such as graphite (G, 10 m² g⁻¹), ribbon-type carbon nanofibers (CNF-R, 109 m² g⁻¹), and carbon nanospheres (CNS, 3 m² g⁻¹), were prepared by the sol–gold method using tetrahydroxymethyl phosphonium chloride as the reducing agent. Different techniques were employed to characterize both the supports and the final Au catalysts: atomic absorption spectrometry, transmission electron microscopy, thermogravimetric analysis, X-ray diffraction, elemental analyses, N₂ adsorption–desorption analysis, temperature-programmed reduction, and temperature-programmed decomposition. Au catalysts were tested in the liquid phase by selective oxidation of both commercial and crude glycerol, the latter obtained from the manufacture of biodiesel. Catalytic results obtained with commercial glycerol showed that the product distribution was dependent on the nature of the support and consequently on the Au particle size. The highest catalyst activity was achieved using highly crystalline carbon supports, supporting small-size (highly dispersed) Au particles. Accordingly the graphite-based catalyst exhibited higher catalytic activity than the CNF-R-based one. Catalytic results similar to those obtained with commercial glycerol were obtained when testing the stream resulting from a low cost neutralization procedure of the crude glycerol.

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1. Introduction

Carbonaceous supports, typically graphite (G), have been widely used in heterogeneous catalysis due to their resistance to acid/basic media, adjustable porosity, surface chemistry and easy recovery of the supported metal by controlled combustion [1,2]. However, the discovery of novel carbon nanostructures, such as carbon nanofibers (CNF) and carbon nanospheres (CNS), has led to growing interest in potential catalytic applications [3–7]. CNF are characterized by high aspect ratio bodies with enhanced mechanical strength and surface areas in the range 10–200 m² g⁻¹ [1,7]. They present a large amount of edges in the lattice and basal regions, providing increased metal–support interactions [7], and lower mass transfer constraints associated with their mesoporous character, in comparison with microporous activated carbons [8]. CNS are typically isolated as a conglomeration of spherical bodies with low surface areas (≈20 m² g⁻¹) [9] but a high surface chemical activity provided by the “unclosed” graphitic layers, reactive open edges and “dangling bonds”, which can enhance reactant adsorption [10]. These carbonaceous supports were very active and selective in a vast

range of oxidation reactions in liquid phase [7,11–17]. However, CNS have been proposed as potential catalyst supports [10,18,19] but there is a dearth of studies dealing with their use in reactions of oxidation. To the best of our knowledge, this work is the first study to be related with the use of CNS as a catalytic support in this kind of reactions.

Glycerol, particularly, is produced as a side product in a transesterification or alcoholysis reaction [20,21]. Actually, the increasing production of biodiesel worldwide has led to oversupply of glycerol in the market. Consequently, the price of glycerol has plummeted significantly and subsequently generates lower side income for biodiesel producer. In this sense, numerous studies have been conducted to revalorize glycerol, especially as a raw material in the manufacture of value-added products via oxidation [22–27].

Selective oxidation of glycerol is considered of interest due to that the glycerol structure lends itself well to catalytic oxidative processes using inexpensive oxidizing agents such as air, oxygen or hydrogen peroxide, producing a number of new derivatives (glyceric acid, hydroxypyruvic acid, glycolic acid, mesoxalic acid, oxalic acid, tartronic acid, etc.) [12]. The majority of these products produced through non-environmentally stoichiometric oxidation processes, poor selectivity or low productivity fermentation processes [24,28,29].

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