Catalytic Oxidation of Crude Glycerol using Au Catalyst Based on Carbonaceous Supports.

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Carbonaceous supports, typically activated carbon (AC) and graphite (G) are widely used in heterogeneous catalysis due to their specific properties, such as resistance to acid/basic media, possibility of controlling porosity and surface chemistry and easy recovery of the metal by burning off the support [1]. The discovery of novel carbon nanostructures, such as carbon nanofibers (CNF), nanotubes (CNT) and nanospheres (CNS), has led to increased activity in terms of catalytic applications. CNF are characterized by high aspect ratio bodies with enhanced mechanical strength and surface areas in the range 10-200 $m^2 g^{-1}$. They present a large amount of edges in the lattice and basal regions, providing increased metal-support interactions, and lower mass transfer constraints associated with their mesoporous character, in comparison with microporous activated carbons. CNS are typically isolated as a conglomeration of spherical bodies with low specific surface area (ca. 20 $m^2 g^{-1}$) but a high surface chemical activity provided by the unclosed graphitic layers, reactive open edges and "dangling bonds" which can enhance reactant adsorption. Therefore, it was considered of interest the study, as catalytic supports, in the selective oxidation of commercial glycerol and crude glycerol, three carbon materials with different morphology and crystallinity, such as graphite (G), Ribbon type carbon nanofibers (CNF-R) and carbon nanospheres (CNS). The interest of this reaction is related to the increasing expansion of biodiesel production, 100 kg of glycerol, as a by-product, is produced per 1 tonne of biodiesel. Glycerol is a highly functionalized compound that could give rise to many compounds such as glyceric acid, hydroxypyruvic acid, glyceric acid, glycolic acid, mesoxalic acid, oxalic acid, tartronic acid, etc. [2]. However, glycerol resulting as a by-product of transesterification process typically contains a mixture of methanol, water, inorganic salts (catalyst residue), free fatty acids, unreacted mono-, di- and triglycerides, methyl esters, and a variety of other organic materials in varying qualities, depending on the biodiesel process [3]. As consequence, crude glycerol, with an estimated 50% purity, has few direct uses and is considered as a low value product. For this reason, the present study was focused in the revalorization of crude glycerol to obtain products of high value. Thus, different Au catalyst based on carbonaceous supports has been tested in the selective oxidation of glycerol of different purity: crude glycerol, crude glycerol purified by evaporation using a vacuum flash process, crude glycerol neutralized with hydrochloric acid and, with comparative ends, commercial glycerol.

CNF-R supports were prepared by the catalytic decomposition of ethylene over Ni/SiO_2 at 1023 K, CNS were synthesized via the pyrolysis of benzene and G support was commercially acquired [4, 5]. The metal function (Au) was supported by the sol-gold method using THPC as oxidizing agent (-SGT). All the supports and catalysts were characterized by the following techniques: N_2 adsorption-desorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), temperature programmed oxidation (TPO), temperature programmed desorption (TPD) and temperature programmed reduction (TPR). Catalytic activity measurements were carried out with oxygen under pressure to 5 bar, 333 K, 300 ml of a 0.3 M glycerol solution, glycerol/Au = 3500 mol/mol, 1000 rpm and NaOH/glycerol = 2 mol/mol.

The physicochemical properties of the supports have been described in detail elsewhere [5, 6]. Table 1 and Figure 1 show how, the nature of support and Au particle size influences on catalytic results. It could be observed as, these two parameters played an important role in the deposition of Au particles and thus, in its catalysis. Both conversion and selectivity increased in decreasing the Au particle size and increasing the metal dispersion. Respect to the nature of the support, it was observed as crystalline materials, such as G, promoted a better anchoring of small and well dispersed Au particles (which facilitates the abstraction of protons of glycerol, increasing conversion) compared to partially crystalline supports such as CNF. By its part, Au catalysts based on CNS, presented a very good dispersion of small Au particles, which favored its catalytic activity. In addition, in all cases, catalytic activity using commercial glycerol was superior respect to the crude glycerol. Nevertheless, after purification of the crude glycerol by neutralization, the catalytic activity was similar to that obtained using the commercial one, suggesting that this could be an interesting low cost alternative to revalorization of crude glycerol to obtain products of high added value.

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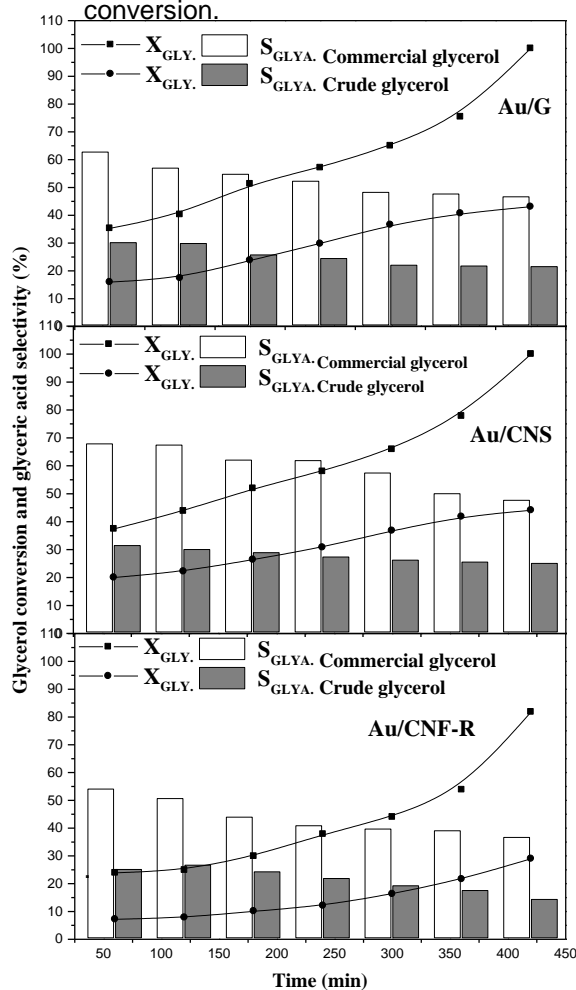[1] P. Serp, M. Corrias and P. Kalck, Appl. Catal. A: General 253 (2003) 337.

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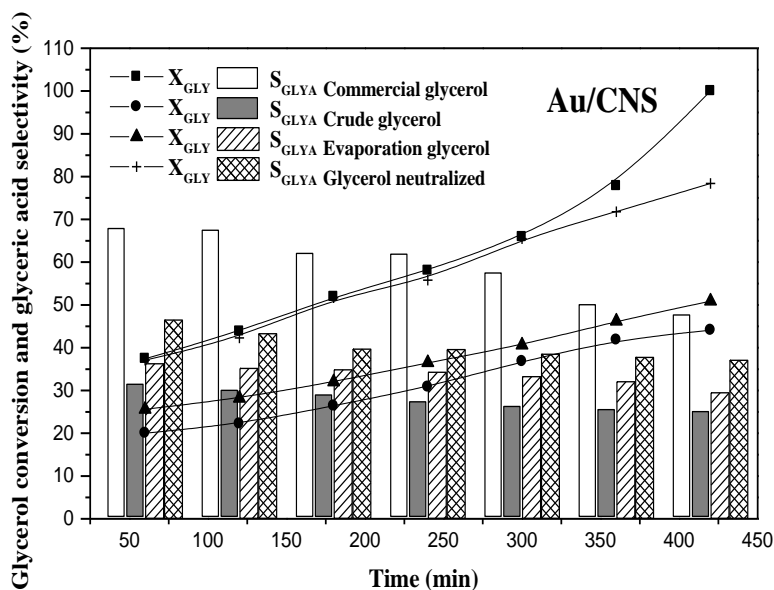
Figures

Table 1. Physicochemical properties of the Au catalysts and influence of support and Au particles size on the selectivity to several reaction products.

	Catalysts	$\bar{d}_s$ (nm)	BET surface area ($m^2 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)	d_{002} (nm)	L_c (nm)	Time (h)	S_{GLYA}[a] (%)	S_{MOXALA}[a] (%)	S_{GLYCA}[a] (%)	S_{HPYA}[a] (%)	S_{TARAC}[a] (%)	S_{OXALA}[a] (%)
COMMERCIAL GLYCEROL	Au/G	7.7	9.83	0.019	0.338	321.8	1	62.9	0.0	25.4	3.2	4.1	4.4
	Au/CNF	13.2	104	0.029	0.342	8.75	3	44.1	3.3	37.9	4.3	7.2	3.2
	Au/CNS	4.2	2.54	0.011	0.347	30.53	1	68.0	3.7	24.2	1.4	1.9	0.9
CRUDE GLYCEROL	Au/G	7.7	9.83	0.019	0.338	321.8	5	22.2	4.7	66.2	4.3	2.1	0.5
	Au/CNF	13.2	104	0.029	0.342	8.75	7	14.5	11.1	58.4	11.4	3.2	1.5
	Au/CNS	4.2	2.54	0.011	0.347	30.53	5	26.4	9.2	49.0	6.4	7.7	1.3

[b] Selectivity to glyceric acid (GLYA), glycolic acid (GLYCA), tartronic acid (TARAC), oxalic acid (OXALA), mesooxalic acid (MOXALA) and hydroxypyruvic acid (HPYA), respectively, at 35% of glycerol conversion.

Figure 2. Influence of the purification treatment of crude glycerol: Glycerol conversion and glyceric acid selectivity as a function of time-on-stream.

Figure 1. Influence of the nature of the carbonaceous support: Glycerol conversion and glyceric acid selectivity as a function of time-on-stream.