Influence of support, preparation method and operating condition on the selective oxidation of glycerol

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Introduction

Carbonaceous supports, typically activated carbon, 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 [1]. Therefore, was considered of interest to the study, as catalytic supports the selective oxidation of glycerol, three carbon materials with different morphology and crystallinity, such as graphite (G), activated carbon (AC) and ribbon type carbon nanofibers (CNF-R). The interest of this reaction is due to the increasing expansion of biodiesel production, 100 kg of glycerol, as a by-product, is produced per 1 tonne of biodiesel. Furthermore, glycerol is a highly functionalized compound, giving rise to many compounds (glyceric acid, hydroxypyruvic acid, glyceric acid, glycolic acid, mesoxalic acid, oxalic acid, tartronic acid, etc.) [2]. Actually, the majority of these products are produced using non-environmentally stoichiometric oxidation or low productivity fermentation processes. So, replacement of these processes by friendly environmentally and low cost ones, such as the use of cheap oxidizing agents with the use of heterogeneous catalysts, will be a step forwards. In addition, several authors have shown that both the glycerol conversion and selectivity to glyceric acid, are parameters that depend not only on the properties of the catalyst, but the conditions of operation [2,3]. Therefore, it was considered of interest to propose a study which analyzes the influence of these parameters in the catalytic activity of glycerol.

Experimental

CNF supports were prepared by the catalytic decomposition of ethylene over Ni/SiO_2 at 1023 K [4]. The AC and G used are commercial. The metal function (Au) was introduced on the support by two techniques: impregnation (-IMP) and sol-gold using THPC as oxidizing agent (-SGT). Both supports and catalysts were characterized by the following techniques: N_2 adsorption-desorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectroscopy, temperature programmed oxidation, desorption and reduction (TPO, TPD, TPR, respectively). The catalysts prepared were tested in the selective oxidation of glycerol. Thus, it was studied the influence of the catalyst preparation method, nature of support and different reaction conditions (pressure, temperature, molar ratio NaOH/glycerol and stirring speed) on the catalytic activity (conversion and selectivity to glyceric acid). A kinetic model, based algorithm the Levenberg-Marquardt method, was proposed.

Results/Discussion

The physicochemical properties of the supports have been described in detail elsewhere [5]. Table 1 shows how, the nature of support and catalyst preparation method influenced on the achieved catalytic results. We observed that these two parameters played an important role in the deposition of Au particles and thus, in its catalysis. Both conversion and selectivity increased with decreasing gold particle sizes (higher dispersion). Catalysts, where gold was supported by the gold-sol method, were more active and selective than those prepared by the precipitation method. As to the nature of the medium, it was observed as in the case of the supports based on G and CNFs (both crystalline materials), Au particles were better anchored and more dispersed, which facilitates the abstraction of the protons of glycerol, increasing the conversion. However, Au-based catalysts supported on AC, even though they had a good dispersion as consequence of the high specific surface area, showed lower catalytic activity due to the weak metal (Au)-support interaction.

Table 1. Influence of support and preparation method.

Catalysts/ Method	$\overline{d}_s$ (nm)	TOF [1] (h^{-1})	S_{GLYA} [2] (%)	S_{GLYCA} [2] (%)	S_{TARAC} [2] (%)	S_{OXALA} [2] (%)	S_{MOXALA} [2] (%)	S_{HPYA} [2] (%)
Au/G-IMP	12.6	821.5	52.1	33.5	5.2	4.4	3.1	1.7
Au/G-SGT	7.7	1280.8	62.9	25.4	4.1	4.4	0	3.2
Au/AC-IMP	13.3	437.6	11.3	54.2	7.6	7.2	15.1	4.6
Au/AC-SGT	7.8	645.4	37.1	43	6.9	4	3.3	5.7
Au/CNF-R-IMP	19.2	630.2	33.7	47.1	6.3	4.4	5.8	2.7
Au/CNF-R-SGT	13.2	866.2	41	40.8	6.6	3.3	4.3	4

[1] Value of TOF (h^{-1}) after 1 h of reaction.
[2] Selectivity of products at 35 % conversion of glycerol.

Finally, several studies carried out by varying the pressure (3, 5 and 8 bar) and temperature (298, 307.8, 333 and 373 K), showed how, an increase in the oxygen pressure not drastically affected the conversion of glycerol, but favoured the selectivity to glyceric acid. This can be attributed to that a pressure increase minimized the formation of hydrogen peroxide, with the subsequent decrease in the formation of glycolic acid [3]. As for temperature, an increase of the same resulted in a significant increase in the catalytic activity, favouring the oxidation of glycolic and tartronic acid to oxalic acid, resulting in an increase in selectivity to glyceric acid [2].

References

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