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SiO_2-, Cu-, and Ni-supported Au nanoparticles for selective glycerol oxidation in the liquid phase

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ABSTRACT

We tested for the first time the efficiency of SiO_2-, Cu-, and Ni-supported Au in deep glycerol oxidation in a diluted and viscous H_2O_2/H_2O liquid phase. Acetic acid (AA), the C_2 oxidate, was preferentially formed in such a system. High conversion (100%) and AA yields (90%) were observed for the sol–gel SiO_2-supported Au in diluted solutions. Although with the increase of glycerol concentration in the viscous liquid phase these values decreased to ca. 40% (conversion) and 20% (AA yield), the addition of acetonitrile improved the AA yield to ca. 40%, while the surfactants were found to be capable of a many-fold enhancement of the catalyst activity at the room temperature highly viscous liquid phase. High performances were also observed for the bimetallic Au/Cu and Au/Ni catalysts obtained by nano-Au transfer; however, these catalysts were destroyed during the reaction by the Cu or Ni leaching effect.

1. Introduction

Renewable naturally sourced carbohydrates, amino acids, and triglycerides are available in vast quantities in our environment. This biomass, a product of living organisms, could be used as valuable feedstock for chemical processing; however, we need *novel chemistry to transform large amounts selectively and efficiently in their natural state without extensive functionalization and protection* [1]. For this reason, biomass conversion has received increasing attention in contemporary chemistry. Glycerol yielded as a by-product in biodiesel production is one of the most widely-available biosourced chemicals, making it an attractive target of investigations. The oxidation of glycerol could yield a variety of C_1 to C_3 oxygenates, which are potentially valuable chemicals in chemical and pharmaceutical applications or intermediates in organic synthesis. This has triggered a growing interest in new methods for this process. Although there has been tremendous progress in recent years in this area, a number of problems remain to be solved [2,3]. Available enzymatic or stoichiometric methods are often wasteful and economically inefficient. Alternatively, a variety of catalytic reactions have been developed; e.g., catalytic glycerol conversions have been thoroughly reviewed [4]. Nanocatalysis is an interesting option in this area.

Nanocatalysts are extremely sensitive toward structure differentiation, and their activity and selectivity depend not only on nanometal and support type but also on size, shape, and composition [5]. Thus, optimization of such materials is an open issue. In fact, more efficient catalysts are still being sought to run the reactions with higher yields and higher selectivity under mild conditions. Other important problems to be addressed include reducing the fraction of noble metals, facilitating the catalyst separation, improving reusability, and reducing contamination of the final products. Gold nanoparticles (Au NPs) catalyze a variety of reactions [6–9]. As they tend to agglomerate, they are usually supported on carriers to form more stable catalytic systems. Generally, Au NPs are available on a variety of supports, from carbon-like graphite to inorganic materials. Basically, the first should be wettable by apolar reagents and solvents, while the latter should be wettable by polar ones. Wettability, and consequently catalyst availability for the reactants, is of crucial importance for the reaction progress; e.g., the recently oxidation of cyclohexene and D-glucose over nano-Au/SiO_2 in water has been compared. In this reaction, polar polyhydroxyl D-glucose complying with polar SiO_2

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support and a polar solvent (H_2O) reacted smoothly at room temperature, whereas nonpolar cyclohexene violating the polarity rule needed the addition of surfactants to react efficiently [10].

Glycerol oxidation catalyzed on Au NPs, pioneered by Hutchings et al. [11,12], has been exhaustively studied recently [8,9,13–17]. Possible glycerol oxidates can be connected by a complex reaction network [3,16,21]. Scheme 1 presents a variety of products yielded from such catalytic systems, with nanometals supported on carbon or inorganic carriers. The C_3 oxygenates, of which dihydroxyacetone is the most desired product, designate oxidation without C–C cleavage. Possible products and catalytic systems are specified in Tables 15 and 16 of Ref. [3]. In contrast, oxidation to C_2 has been investigated as a potential source of glycolic acid [18] and C_1 products. In turn, CO_2 and HCOOH are products of the highest chain decomposition level.

Glycerol oxidation by aqueous hydrogen peroxide in an autoclave reactor on Au/C, Au/graphite, or Au/TiO_2 under the presence of NaOH provided a mixture of glycolate, glycerate, and tartronate [18]. Moreover, oxidation of glycerol to glyceric acid using an Au/graphite system in aqueous sodium hydroxide under basic free [19] or mild conditions [11] also appeared to be relatively selective. The influence of various carbonaceous supporting materials on the Au/C catalyst performance in glycerol oxidation was described by Gil et al. [20]. More generally, the influence of various support materials on catalytic glycerol oxidation was reviewed by Katryniok et al. [16].

In this study, we tested the efficiency of the deep oxidation of glycerol in the presence of unmodified silica-supported nanogold catalyst in aqueous 30% hydrogen peroxide, under mild conditions in aqueous glycerol solutions of various dilutions. We assumed that polar glycerol or a glycerol/water mixture would prefer a relatively hydrophilic catalyst carrier, which should provide the widest wettability and availability for the reacting molecules. This would be especially important for highly viscous undiluted glycerol solutions. Thus, a suspension of the silica-supported catalyst should provide a system in which the reaction proceeds smoothly, while hydrogen peroxide could be a compatible convenient, safe, and green reagent in such a system. It is also a model oxidant, since it was reported that aerobic oxidation on Au NPs proceeds with in situ formation of H_2O_2 [16]. To the best of our knowledge, the oxidation of glycerol on SiO_2-supported nano-Au has never been investigated, despite the polarity match between glycerol, SiO_2, and H_2O_2/H_2O systems. Recently, we reported a new method for transferring SiO_2-supported nanometals to a variety of other supports [22]. As Au/Cu nanoparticles have been recently developed as an interesting catalyst for the oxidation of various alcohols [23], here we prepared bimetallic nano-Au supported on Cu or Ni grains, to test their performance in glycerol oxidation. Despite the complex network of possible reactions (Scheme 1), a process of deep glycerol oxidation proceeds on the investigated catalysts preferentially to acetic acid (AA).

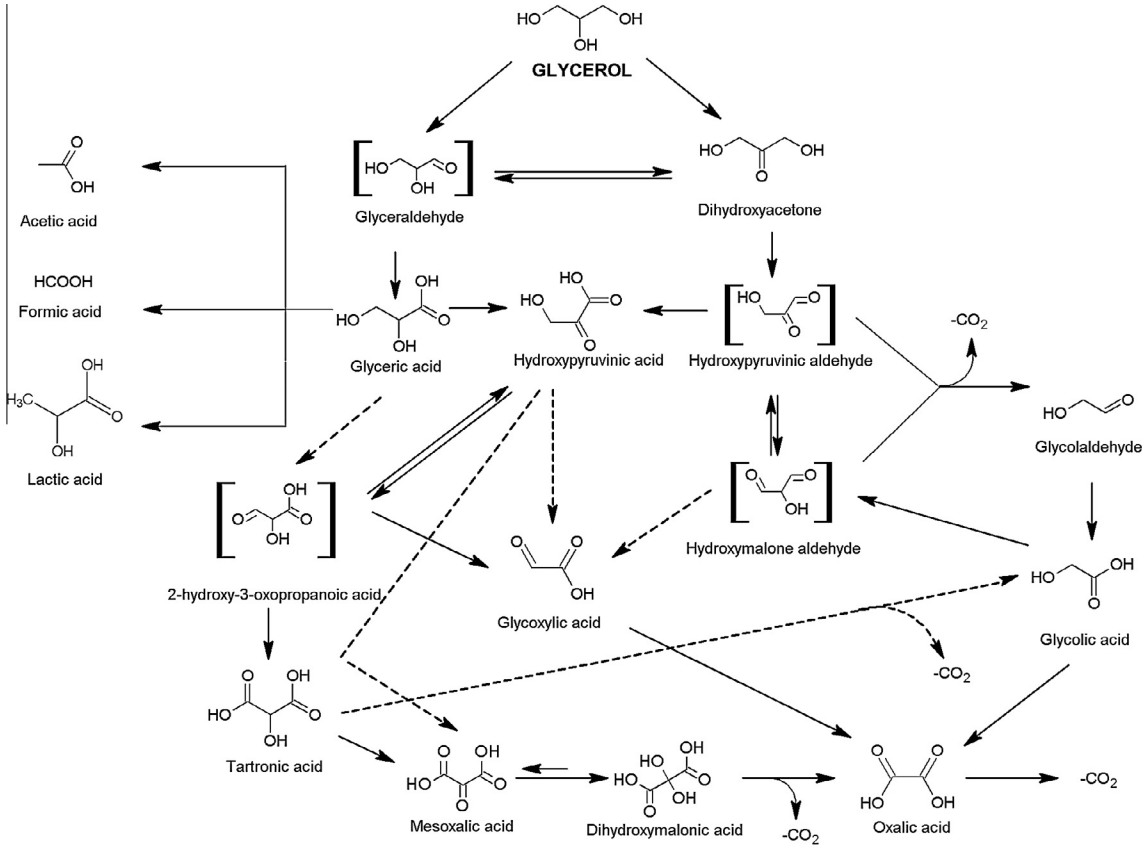
2. Experimental

2.1. Preparation of Au NPs on silica or Cu and Ni carriers

The series of nanocatalysts, namely Au/silica or Au/Cu and Au/Ni were prepared according to the procedure optimized (for details see: Supplementary material).

2.2. Glycerol oxidation

Nano-Au catalyst (20 mg, 0.2–20.0 μmol Au) was suspended in a mixture of 1.0 mL of 30% hydrogen peroxide (10 mmol H_2O_2) and



Scheme 1. A complex reaction network of glycerol oxidation [16].