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Glycerol oxidation over gold supported catalysts – "Two faces" of sulphur based anchoring agent

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ABSTRACT

Three different alumina-supported catalysts were prepared according to 3 different methods, aiming at achieving fine deposition of gold particles. In methods 1 and 2, (3-aminopropyl)triethoxysilane (APTES) and (3-mercaptopropyl)triethoxysilane (MPTES) were respectively used as anchoring agents. In method 3, the gold particles were directly deposited on the support without using any anchoring agent. The performances of the so-obtained catalysts were evaluated in the reaction of glycerol partial oxidation in the liquid phase, and compared to those of a 1 wt.% Au/Al_2O_3 catalyst provided by Mintek. The best catalyst A3 (method 3) exhibited a 99% conversion at 60 °C after 2.5 h, with glyceric and glycolic acids selectivities of 60 and 20%, respectively. These performances were slightly higher than those of the reference commercial catalyst (95% conversion with glyceric and glycolic acids selectivities of 62 and 20%, respectively). In the case of A2 catalyst (method 2), in spite of very good dispersion of small nanoparticles on the surface, which is normally supposed to yield very active materials, a very strong inhibition of glycerol conversion was observed. After 2.5 h of process at 60 °C, the glycerol conversion did not exceed 4%. A similar behavior was also observed for TiO_2- and ZnO-supported catalysts, prepared in the same manner (using MPTES). In order to get a better understanding of the parameters ruling the reactivity of the various catalytic systems, a series of experiments over the commercial catalyst was performed, in which small quantities of various sulphur derivatives and antioxidants were used in the reaction mixture to simulate the response of the various species that can be present in the lab-prepared samples (method 2). The results, together with XPS analysis, suggests that there are three possible interpretations of the observed inhibition effect: (i) a strong interaction between gold and sulphur leading to the formation of covalent Au—S bonds on nanoparticle's surface; (ii) the formation of so-called SAM's (self-assembled monolayers) blocking access to surface active centers; or (iii) an inhibition of the reactivity due to antioxidation properties of S-derivatives.

1. Introduction

Nowadays, it is believed that the glycerol can be a potentially important biorefinery feedstock [1,2], and its transformation by chemical or biochemical processes has thus attracted a lot of scientific attention in the last decades [1–5]. Oxidation in the liquid phase is an example of catalytic process that opens perspectives for converting glycerol to highly valuable products, such as glyceric acid, tartronic acid, glycolic acid, oxalic acid, dihydroxyacetone, or glyceraldehyde [1–4]. From the abundant literature, it appears that, so far, platinum, palladium, and especially gold-supported catalysts show very high activity in this process. It is also well known that their catalytic performances (and especially selectivity) are largely influenced by the preparation method and the selected reaction conditions [1,2,5–7].

Concerning gold-based catalysts, it is generally admitted that a proper selection of the support [8–10], of the gold precursor type [11], of the selected technique for particles deposition

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(impregnation, deposition–precipitation, use of an anchoring agent, etc.,) [1,7,12–14], as well as of the method and the conditions of the final steps of synthesis (drying and thermal or chemical reduction of the gold precursor [15–17]), has a significant influence on the properties of the final material. XPS (X-ray photoelectron spectroscopy) and TEM (transmission electron microscopy) are largely used to reliably characterize such solids, as both techniques give complementary valuable information about the chemical state of gold (Au^{3+}/Au^0) and about the diameter of the deposited particles, respectively, which are key parameters governing the gold-based catalysts reactivity [1,5–7]. The results brought by elemental analysis are also of specific interest, since they straightforwardly enable the assessment of the actual amount of supported gold, which is an indicator of the preparation method efficiency, accuracy, and precision.

Based on our previous experiences on finely controlled anchoring of gold nanoparticles in capillaries [18] and after examining the literature, especially the review of Daniel and Astruc [19] describing the formation of self-assembled monolayers (SAM's) and very well defined and arranged gold nanoparticles obtained using various derivatives, we selected and used APTES and MPTES as an anchoring agents for immobilization of reduced gold nanoparticles on an alumina surface. The third method used in this work was the direct deposition of the gold precursor on the alumina support followed by its chemical reduction in solution. The benefit of these methods is that they all allow the preparation of catalysts by a simplified "one-pot" procedure, which is thus an environmental friendly greener way and can have a large importance on the assessment of the catalysts competitiveness, especially referring to the commercial materials. In the present work, the AUROlite™ gold catalyst had been used as a reference, standard system (like already performed in several projects [20,21]), since it is considered as one of the most active materials.

The main goal of our work was to compare usability of various anchoring agents for preparing fine gold-supported catalysts by simplified "one-pot" procedures, and testing their activity in the glycerol oxidation process. However, as our preliminary studies showed a strong inhibition of glycerol conversion while using catalysts prepared with MPTES, we decided to get deeper insights on this topic and present herein the possible explanations for this phenomena.

According to the literature, very strong inhibition of the oxidation reaction over the catalysts prepared using MPTES as an anchoring agent could be explained by different hypotheses: (i) the thiol-based derivatives are known for their antioxidant activity in medicine, biochemistry, and oleochemistry [22–25], especially for the free-radical processes. On the other hand, (ii) it is well known that the basic conditions are preferable for glycerol oxidation over gold catalysts, so the acidic properties of —SH groups present on the catalyst surface may attenuate the activation step expected by the base addition (here NaOH). Finally, (iii) the strong affinity between gold and sulphur resulting in a change in electronic properties of gold (covalent bond formation) enables formation of self-assembly 2D monolayers, the so-called SAM's, typical for thiolate compounds [26–29]. Evidences of such monolayers formation can be observed by XPS (shift of the BE of the Au 4f level [27]), and also by TEM (well-organized, symmetrical pattern with hexagonal distribution of surface immobilized AuNPs [30]). Thus, it is highly possible that the formation of a tight coverage of MPTES on the gold surface, which enables the formation of well-dispersed gold particles, can also block the access of reagents to the gold active centers. This aspect of selective site blocking by adsorbed thiolates was discussed in details by Haider et al., studying aerobic oxidation of benzyl alcohol and hydrogenation of ketopantolactone [31]. Also, Quantanilla et al. reported the effect of surface blocking by adsorption of weekly bounding capping agents (dodecylamine and PVP used in 10–35 molar excess to gold) [32], while Della Pina et al. working on gold-catalyzed aerobic oxidation of glucose pointed the alteration of the electronic properties of the gold by small amounts of thiol derivatives, as the main factor deciding about inhibition of the reaction [33]. Nevertheless, most of the works deal with the situation where the potential "poison" is added to the reaction mixture together with the reagents and standard gold supported catalyst.

Herein, we compare the aforementioned hypothesis, and on the basis of a series of experiments we evaluate their impact on the glycerol oxidation reaction.

2. Materials and methods

2.1. Materials used in the work

All the chemicals were used as received without any further purification. Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4$) was purchased from Alfa Aesar, and sodium borohydride ($NaBH_4$) 99% from Acros Organics. An alumina oxide powder (Al_2O_3) purchased from MERCK was used as a support, while APTES 99% from Aldrich and MPTES 99% purchased from Alfa Aesar were used as anchoring agents.

Anhydrous glycerol 99% ($C_3H_8O_3$) and purum sodium hydroxide (NaOH) from Sigma–Aldrich were used for the catalytic tests. The used eluent for liquid chromatography was prepared from HPLC-grade solvents: 0.25 M H_2SO_4 from Fluka, deionized water and CH_3CN from Sigma–Aldrich. All the solutions were prepared in distilled water (filter system: AUTOSTILL 4000X).

The reference 1 wt.% Au/Al_2O_3 catalyst (AUROlite™, batch BC17 labelled here K1) was received from Mintek, while 1 wt.% Au/TiO_2 and 1 wt.% Au/ZnO (named here K2 and K3, respectively) were received from World Gold Council.

Zinc oxide from Merck and titanium oxide from Degussa were used as a support for the preparation of Au/ZnO and Au/TiO_2 series of catalysts.

For supplementary tests in the presence of sulphur derivatives, we used (3-mercaptopropyl)trimethoxysilane (MPTMS) from Aldrich, and thiophene as well as thioglycolic acid from Fluka. In the case of the use of antioxidants, we used the commonly employed butylated hydroxytoluene (BHT) and gallic acid from Aldrich.

2.2. Catalysts preparation methods

All the catalysts were prepared by a simplified "one-pot" procedure. In the first method, APTES was used as an anchoring agent (method 1, catalyst A1): In a round-bottom flask, 1 g of alumina support was suspended in 200 cm^3 of distilled water, and then APTES was added (molar ratio of APTES/Au = 2). The solution was then refluxed for 3 h at 80 °C. Next, the gold precursor solution ($HAuCl_4$) was added to the suspension in order to obtain the final catalyst with a total theoretical gold loading of 1 wt.%. To achieve a pH value between 5 and 7, a sodium hydroxide solution was used. After 1 h of continuous agitation and reflux at 80 °C, 1 cm^3 of reducing agent solution (containing 10 mg of $NaBH_4$) was added to the mixture, which resulted in an immediate change in color of the solution from yellow (characteristic for the gold precursor $HAuCl_4/Au^{3+}$) to dark brown, which gives a direct visual indication of the gold precursor reduction ($Au^{3+} \rightarrow Au^0$). The final mixture was maintained for an additional 2 h under heating and mixing. Finally, the solid was filtrated on a Büchner funnel type 3, washed with 200 cm^3 of distilled water, and then dried in static air at 100 °C for 12 h.

In the second method, MPTES was used as an anchoring agent (method 2, catalyst A2), while in the third method (method 3, catalyst A3), no anchoring agent was used and the gold particles were