



Bismuth modified Au-Pt bimetallic catalysts for dihydroxyacetone production



Alberto Villa^a, Sebastiano Campisi^a, Carine E. Chan-Thaw^a, Davide Motta^a,
Di Wang^b, Laura Prati^{a,*}

^a Università degli Studi di Milano, Dipartimento di Chimica, via Golgi 19, I-20133 Milano, Italy

^b Institut für Nanotechnologie and Karlsruhe Nano Micro Facility (KNMF), Karlsruher Institut für Technologie, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

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ABSTRACT

Bi has been employed as a modifier for AuPt/AC alloy based catalysts for the base-free glycerol oxidation. The addition of Bi has a significant effect on the selectivity of the reaction. Indeed, in the absence of Bi, the oxidation of the primary alcohol function is favored with the production of glyceric acid as main product. On the contrary, the addition of Bi promotes the oxidation of the secondary OH function leading to the production of dihydroxyacetone (DHA) as the main product (selectivity of 63% at 80% conversion). Differently from the gold-free catalyst Bi-Pt/AC, which suffers from Bi leaching, the Au modified one, namely Bi-AuPt/AC, enhances the catalyst stability by limiting the Bi leaching thus resulting in a good selectivity to DHA even at high conversion.

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1. Introduction

Glycerol represents a well-studied substrate, in view of its importance as a cheap and renewable material derived from biomass, on which a new chemical platform can be based [1–3]. In particular, high value fine chemicals can be obtained from the oxidation of glycerol, as for example glyceric acid (GLYAC), tartronic acid (TA), hydroxypurivic acid (HPA) and dihydroxyacetone (DHA) as pictured in Scheme 1 [1–3]. Among them, DHA is economically the most interesting product due to its application in the cosmetic industry as a tanning agent. DHA is currently industrially produced by biological fermentation processes [4,5]. In the last years, many studies were devoted to find alternative, environmentally friendly methods typically involving the use of molecular oxygen as the oxidant in the presence of a heterogeneous catalyst [6–13]. Kimura's group was the first to show that Pt/AC in an acidic media is able to produce DHA deriving from the oxidation of the secondary hydroxyl group of glycerol, even in low yield (4%) [6]. Similar results were obtained with Pt on CNTs (maximum yield 6%) and it was highlighted that the selectivity of the reaction depends on the particle size [14]. It was also discovered that the addition of a promoter, in particular Bi, was able to increase the yield to

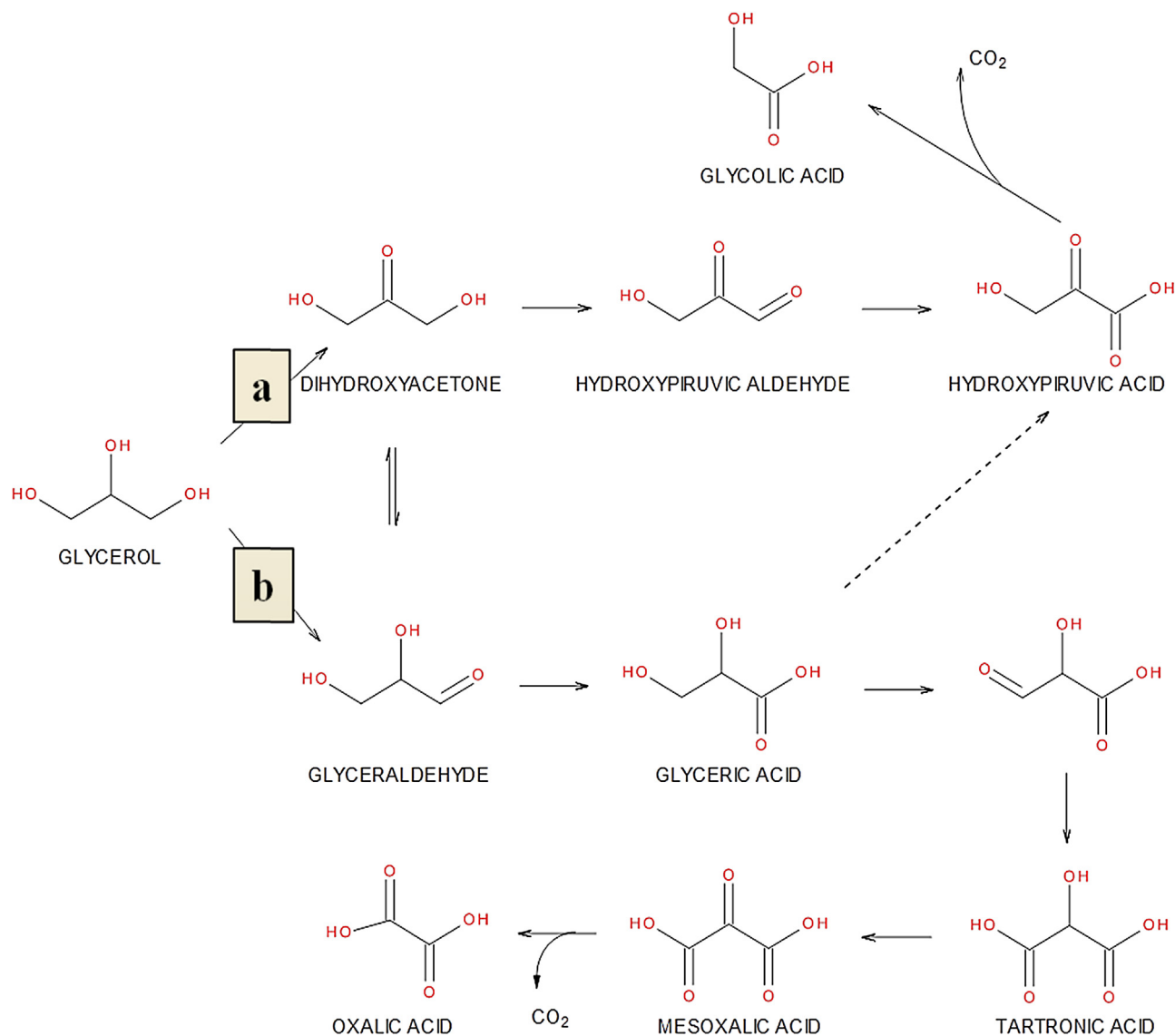
DHA [7–9]. In particular it was disclosed that bismuth acts as site blockers on Pt(111), controlling the geometry of glycerol adsorption and favoring the oxidation of the secondary group [9]. These studies also reported that the Bi/Pt ratio has an important impact on the catalytic performance [9–11] showing that a yield of 35% of DHA was obtained when Bi/Pt ratio is not more than 0.2 [9].

However, these studies also showed that Pt/Bi systems suffer from deactivation showing a drop of selectivity to DHA at high conversions. These phenomena can be probably ascribed to the strong chelating properties of glycerol and of its oxidation products in acid media that can block the active sites as well as leach the metal into the solution. Indeed, the leaching of Bi during the reaction was accepted to be responsible of the drop of selectivity to DHA.

Claus et al. showed that also Au is able to catalyze the oxidation of glycerol to DHA in basic media [13]. However, they obtained a maximum DHA yield of 6.6% most probably due to its low stability under these reaction conditions.

More recently, the effect of the pH in DHA production from glycerol has been investigated with Au supported on different oxides [15]. In particular, a selectivity of 80% to DHA at 20% of conversion in base-free conditions has been reported using Au on CuO. On the contrary, in the presence of NaOH all the catalysts produced sodium glycerate as the main product instead of DHA. In this case, DHA was never detected among the products. Therefore, in agreement with the studies reported on Bi-Pt systems, an acid-neutral environment should be used in order to maximize the DHA production.

* Corresponding author. Tel.: +39 02 503 14357; fax: +39 02 503 14405.
E-mail address: Laura.Prati@unimi.it (L. Prati).



Scheme 1. Reaction scheme for glycerol oxidation.

In the present paper, we focused our attention on the design of catalyst to improve the DHA production taking advantage of previous knowledge about the beneficial effect of the addition of Au to Pt in terms of catalyst life and Bi to Pt in terms of selectivity to DHA.

Indeed, we recently reported that alloying Au to Pt, it is possible to increase the catalyst life, which represents the actual main drawback of Pt and BiPt catalysts reported for the base-free glycerol oxidation [16,17]. Therefore, in order to tune the selectivity to DHA, AuPt catalyst has been modified by the addition of different amount of Bi (0.1 and 1 wt%), using a procedure that we previously reported [18]. The aim of our studies is to investigate both the effect of the Bi addition to AuPt/AC catalyst on the selectivity and in particular the enhancement of stability of Bi-AuPt/AC system compared to the classical Bi-Pt/AC catalyst used for this reaction. Finally, the effect of using Pd instead of Pt has been also considered.

2. Experimental

2.1. Materials

NaAuCl₄·2H₂O, Na₂PdCl₄, K₂PtCl₄ and BiO(NO₃) were from Aldrich (99.99% purity) and activated carbon from Camel (X40S;

SA = 900–1100 m²/g; PV = 1.5 mL/g; pH 9–10). 5% Pt/AC and 1% Bi-5%Pt/AC were from Johnson Matthey. NaBH₄ of purity >96% from Fluka, polyvinylalcohol (PVA) (M_w = 13,000–23,000 87–89% hydrolysed,) from Aldrich were used. Gaseous oxygen from SIAD was 99.99% pure.

2.2. Catalyst preparation

2.2.1. Au-M/AC

AuPt/AC and AuPd/AC have been synthesized following the procedure reported in [19]. In brief, NaAuCl₄·2H₂O was dissolved in 60 mL of H₂O, and PVA (1 wt%) was added (Au/PVA = 1:1, w/w). The yellow solution was stirred for 3 min, after which 0.1 M NaBH₄ (Au/NaBH₄ = 1:4, mol/mol) was added under vigorous magnetic stirring. The ruby-red Au(0) sol was formed immediately. Within a few minutes of sol generation, the gold sol was immobilized by adding the support (acidified to pH 2 by sulphuric acid) under vigorous stirring. The amount of support was calculated as having a gold loading of 0.6 wt% for AuPt/AC and 0.73% for AuPd/AC. After 2 h, the slurry was filtered and the catalyst washed thoroughly with distilled water (neutral mother liquors). The Au/support was dispersed in 40 mL of water, with K₂PtCl₄ or Na₂PdCl₄ and PVA

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