ARTICLE IN PRESS

Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

An investigation on AuPt and AuPt-Bi on granular carbon as catalysts for the oxidation of glycerol under continuous flow conditions

Davide Motta[a], Felipe J Sanchez Trujillo[a], Nikolaos Dimitratos[a], Alberto Villa[b], Laura Prati[b,*]

[a] *Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK*
[b] *Dipartimento di Chimica, Universitá degli Studi di Milano, Via Golgi 19, 20133, Milano, Italy*

ARTICLE INFO

Keywords:
Glycerol oxidation
Hydroxyacetone
Glyceric acid
Continuous flow reactor
Gold-platinum
Bismuth

ABSTRACT

AuPt/AC and Bi modified AuPt/AC were prepared by impregnation using activated granular carbon as support followed by chemical reduction. The catalysts were characterized by means of Atomic Absorption Spectroscopy (AAS), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The catalysts were evaluated in the base free glycerol oxidation at mild reaction conditions in a continuous flow fixed bed reactor. Experimental parameters, such as, contact time (Liquid Hourly Space Velocity: LHSV), temperature and O_2 flow have been varied in order to evaluate catalytic performance in terms of activity, selectivity and long-term stability. Under optimized reaction conditions AuPt/AC showed a high selectivity to glyceric acid (68.3%) whereas Bi-AuPt/AC promoted the oxidation of the secondary alcohol giving a selectivity to dihydroxyacetone (DHA) of 48.1% at 28% conversion, one of the most promising values reported in the current literature. Long-term catalytic performance was carried out for 80 h and revealed a reasonable good stability of AuPt/AC against deactivation and leaching, whereas structural modification and subsequent changes in the catalytic reactivity were envisaged for Bi-AuPt/AC catalyst.

1. Introduction

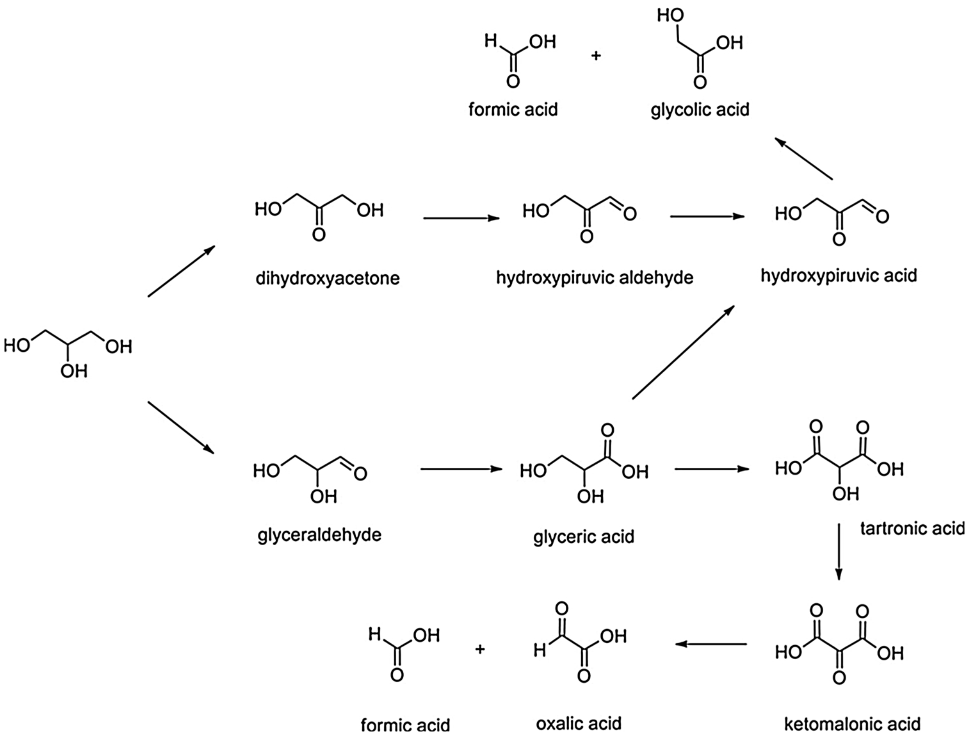
The transformation of glycerol into valuable chemicals and fuels has attracted significant attention in recent years from both academia and industry research groups because of its high potential as a promising bio renewable sustainable chemical building block [1–4]. The annual production of glycerol has been estimated to be higher than 2 million tonnes per year [5] and the main process of production is via the synthesis of biodiesel by the transesterification process using oils and fats with methanol [6]. A range of significant chemical processes have been studied and proposed for the effective transformation of glycerol to a variety of valuable chemicals, such as dihydroxyacetone, glyceraldehyde, glyceric acid, glycolic acid, tartronic acid, hydroxypyruvic acid, lactic acid, acrylic acid using oxidation/dehydration processes (Scheme 1) [7–10]. Due to the diverse range of products one of the main challenges is to control activity, selectivity and stability during the chemical process. Several strategies have been employed to control product selectivity and activity based on the use of bimetallic and trimetallic nanoparticles [11]. Bimetallic Au-Pd, Au-Pt and trimetallic (Au-Pd-Pt) catalysts have shown to be more active than their monometallic counterparts, and achieving high selectivity for the selective production of glyceric and tartronic acids with improved stability in particular under mild base-free conditions [12–19]. One of the most desired and challenging intermediates of the glycerol oxidation process is the selective production of dihydroxyacetone, which is a primary product of the glycerol oxidation process [20]. Dihydroxyacetone is a valuable product extensively used in cosmetic, chemical and pharmaceutical industries and the industrial production of dihydroxyacetone is based on utilization of biocatalytic approaches with yields reaching 90% [21–23]. However, biocatalytic systems are working at specific reaction conditions and are sensitive to variation of experimental conditions, such as, pH, temperature and scale-up production. On the contrary, chemical heterogeneous catalysts and especially Pt- based ones offer the possibility to selectively oxidise glycerol at a range of broader experimental conditions but with lower yield to the desired products due to deactivation issues. Catalytic performance can be also affected from deactivation, poisoning and leaching of active sites even the separation of products is easier than from an enzymatic broth. Previous reports have shown that Pt-based catalysts with the addition of Bi or Sb as promoters are promising approaches to produce dihydroxyacetone with significant levels of conversion and selectivity [24–29]. Recently we have reported the successful utilization of Bi-AuPd/C and Bi-AuPt/C catalysts synthesized by colloidal methods [30,31] for improving the selectivity in a range of alcohol and polyol oxidation

---

[*] Corresponding author.
E-mail address: Laura.Prati@unimi.it (L. Prati).

http://dx.doi.org/10.1016/j.cattod.2017.10.012
Received 6 August 2017; Received in revised form 19 September 2017; Accepted 12 October 2017

Please cite this article as: Motta, D., Catalysis Today (2017), http://dx.doi.org/10.1016/j.cattod.2017.10.012



Scheme 1. Reaction scheme for glycerol oxidation.

reactions. In the case of glycerol oxidation and using a batch reactor configuration system and base-free conditions, we demonstrated the enhanced production of dihydroxyacetone as the main product with selectivity of 63% at 80% conversion. The synthesized Bi-AuPt/C catalysts showed improved catalytic stability than the Au-free Bi-Pt/C catalyst. Taking into account these promising results we extend our studies using continuous flow processes for exploring further the catalytic performance in terms of selectivity, activity and especially long-term stability of Au-Pt and Bi-AuPt catalysts. A range of experimental parameters have been varied such as contact time (Liquid Hourly Space Velocity: LHSV), temperature and O_2 flow to evaluate the catalytic performance and permit structure-activity investigations for getting insight into reaction pathways and possible role of Bi. Herein, we compared the activity of AuPt/AC and Bi-AuPt/AC catalysts. We demonstrate that the selectivity to glyceraldehyde or glyceric acid using AuPt/AC and to dihydroxyacetone using Bi-AuPt/C could be improved considerably by tuning particular experimental parameters of a continuous flow reactor. Finally, we report and discuss the long term catalytic performance of the AuPt/AC and Bi-AuPt/C, in terms of activity, selectivity, stability taking into account metal leaching and restructuring of active sites.

2. Experimental section

2.1. Materials

$NaAuCl_4 \cdot 2H_2O$, K_2PtCl_4 and $BiO(NO)_3$ were from Aldrich (99.99% purity) and granular activated carbon (grain diameter 2–3 mm) ZM 85 W from Camel Chemicals. Before use the carbon was suspended in HNO_3 6 M to remove all metal impurities and ashes and left under stirring for 12 h, then washed several times with distilled water by decantation until the pH of the solution reached values of 6–6.5. Finally, the carbon was filtered off and dried for 5–6 h at 150 °C in static air. $NaBH_4$ of purity > 96% from Fluka, was used. Gaseous oxygen from SIAD was 99.99% pure.

2.2. Catalyst preparation

2.2.1. AuPt/AC

Solid $NaAuCl_4 \cdot 2H_2O$ (0.031 mmol) and K_2PtCl_4 (0.020 mmol) were dissolved in 100 mL of distilled H_2O. Granular activated carbon (1 g) was added to the solution under stirring. The amount of support was calculated as having a metal nominal loading of 5 wt% with Au/Pt molar ratio of 8/2. The mixture was continuously stirred at room temperature for 2 h till the solution turned from pale yellowed to colorless indicating full adsorption of the metal precursors on the support. The carbon was filtered and the solution was studied by AAS to determine the real metal loading. The solid was redispersed in 100 mL of distilled water and a 0.1 M fresh solution of $NaBH_4$ (metal/$NaBH_4$ = 1:4 mol/mol) was added under stirring for a period of 30 min. The catalyst was filtered, thoroughly washed with distilled water (2 L) and dried at 100 °C in static air for 2 h. The catalyst has been labeled as AuPt/AC.

2.2.2. Bi-AuPt/AC

Bismuth was added to a portion of AuPt/AC prepared with the methodology reported above. $BiO(NO)_3$ (0.012 mmol) was dissolved in 100 mL of distilled water at pH = 2 (pH modified using concentrated H_2SO_4). Bi amount was calculated in order to have a final nominal loading of 0.5%. AuPt/AC was added to the solution and left under stirring for 2 h. The slurry was filtered and the solution was studied by AAS to determine the real metal loading. The solid was redispersed in 100 mL of distilled water and a 0.1 M fresh solution of $NaBH_4$ (metal/$NaBH_4$ = 1:1 mol/mol) was added under stirring. The catalyst was filtered, thoroughly washed with distilled water (2L) and dried at 100 °C in static air for 2 h. The catalyst has been labeled as Bi-AuPt/AC.

2.3. Catalytic test

Fixed bed reactor design: a reactor made by Pyrex with an inner diameter of 10 mm and a height of 100 mm, equipped with feed lines for supplying aqueous solution of glycerol (5 wt%) and molecular