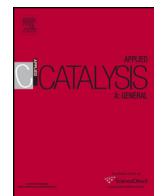




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Insights into the reaction mechanism for 5-hydroxymethylfurfural oxidation to FDCA on bimetallic Pd–Au nanoparticles

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ABSTRACT

This work deals with the oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA) in water using supported Pd–Au nanoparticles. The active phase composition was shown to be crucial for FDCA formation. Indeed, both Au and Pd monometallic nanoparticles formed 5-hydroxymethyl-2-furancarboxylic acid (HMFCFA) under the studied conditions; however, with Pd nanoparticles HMFCFA was not further transformed, while Au and bimetallic Pd–Au systems both catalysed its oxidation to FDCA.

The thermal treatment of Pd–Au catalysts considerably modified their catalytic activity, because Pd atoms migrated and concentrated onto the outer part of bimetallic nanoparticles. The resulting active phase morphology showed a different reaction path for FDCA formation compared to the untreated catalyst, with an important contribution of the Cannizzaro reaction. PVP-protected Pd–Au nanoparticles with different structures (either alloy or core-shell morphology) were synthesized and their reactivity tested in order to confirm the presence of different mechanisms for HMF oxidation, depending on whether the active phase preferentially exposes either Pd or Au atoms.

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1. Introduction

Biomasses are currently the most promising alternative to fossil sources for the production of fuels and chemicals [1,2]. In the transformation of biomass into chemicals, an important role is played by furfural derivatives that have functional groups in position five [3,4]. For instance, 5-hydroxymethyl-2-furfural (HMF) is a key precursor for the synthesis of derivatives with application in the pharmaceutical and polymer industries [5–8]. This molecule can be oxidized to obtain 2,5-furandicarboxylic acid (FDCA), a monomer for the synthesis of a new class of polymers, alternative to those obtained from terephthalic acid. As an example, Avantium is using FDCA to produce polyethylene furandicarboxylate (PEF); the exact route for the synthesis of FDCA has not yet been disclosed, but the current technology for terephthalic acid production using metal/bromide catalysts is probably being evaluated. One

drawback of these catalytic systems is the use of corrosive media and dangerous compounds, which make the process polluting [9–11]. Moreover, there are concerns regarding the purity of both the product and the final polymer.

Recently, Au-supported catalysts were found to be very active for HMF oxidation to FDCA [12,13]. Many researchers have focused their attention on the study of the best material and reaction conditions for improving FDCA yield [14–17]. So far, catalyst stability and productivity are low, but the possibility to obtain both high product purity and better process sustainability makes this catalyst type highly interesting.

According to the current state of the research, the use of bimetallic catalysts with controlled size and composition may be a promising way to improve catalyst activity and stability [18,19]. In our previous studies [18,20], we synthesized titania-supported Au and Au–Cu nanoparticles by using PVP-stabilized sols with controlled size, structure and composition. Unprecedented catalytic activity and stability were obtained with these catalytic materials in the oxidation of HMF to FDCA.

The combination of Pd and Au was also shown to be very successful in producing active and selective catalysts [19,21]. This bimetallic system has been widely studied for a number of

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different applications [22,23]. In particular, Prati and co-workers [24–26] and Hutchings and co-workers [27,28] have demonstrated that the supported Pd–Au alloy shows excellent performances for many oxidation reactions such as the selective oxidation of alcohols and the synthesis of H₂O₂ from H₂ and O₂.

Pd–Au nanoparticles can develop morphologies ranging from core-shell to homogeneous alloys, depending on the method of synthesis and thermal treatment of the catalysts [29]. The Pd–Au alloy most frequently used in catalytic applications contains a bulk Au:Pd molar ratio of 1:1. However, it has been documented that the concentration of the metals at the nanoparticles surface may differ from that of the bulk. Notably, Pd may migrate and concentrate in the outer part of the particles, so developing a core-shell structure [30,31]; this phenomenon may significantly influence the catalytic activity.

In the present study, the role of the active phase and the effect of catalyst calcination were studied for the liquid-phase oxidation of HMF using Pd–Au catalysts. We synthesized nanoparticles with different Pd:Au atomic ratios and morphologies, in order to investigate the effect of these parameters on the catalytic activity and product selectivity.

The results obtained indicate that different reaction paths may take place in the presence of either a homogeneous Pd–Au alloy or of an active phase exposing preferentially monometallic species. Therefore, core-shell nanoparticles were also synthesized in order to investigate on differences in the reaction mechanism due to the formation of a distinct morphology.

2. Experimental

2.1. Materials

The following reagents and products were used for catalyst synthesis and for reactions: polyvinylpyrrolidone (PVP K25, m.w. 29,000 Sigma Aldrich), Sodium hydroxyde (Sigma Aldrich), HAuCl₄·3H₂O (Sigma Aldrich), PdCl₂ (Sigma Aldrich), β-D-Glucose (Fluka), TiO₂ anatase (DT51 Millennium Chemicals), 5-hydroxymethyl-2-furfural (Alfa Aesar), 2,5-furandicarboxylic acid (Toronto Research Chemicals), 5-hydroxymethyl-2-furan carboxylic acid (Toronto Research Chemicals), 5-formyl-2-furan carboxylic acid (Toronto Research Chemicals), 2,5-diformylfuran (Toronto Research Chemicals), and 2,5-Bis(hydroxymethyl)furan (Toronto Research Chemicals).

2.2. Catalyst preparation

Au/TiO₂, Pd/TiO₂, and Pd–Au/TiO₂ catalysts were prepared by the immobilization on the TiO₂ surface of the preformed monometallic and bimetallic colloids. Mono- and bimetallic nanoparticles were prepared using a method previously described [18,20,32–34]. In brief, the necessary quantity of polyvinylpyrrolidone, used as a nanoparticle stabilizer, was added to a solution of NaOH in water. The solution was then heated to 95 °C. At this temperature, β-D-glucose and an aqueous solution containing the metal precursors (HAuCl₄ and PdCl₂) in the desired ratio were

added and stirred for 2.5 min. Some drops of HCl were added to this solution in order to increase the solubility of the Pd salt. The ratio among PVP, β-D-glucose, NaOH, and metals was optimized for each gold and palladium content, taking into consideration the procedure used for other bimetallic systems [35–37]. Core-shell nanoparticles were prepared from a monometallic system (Au or Pd), synthesized following the previous strategy, which had been used as seed for the nucleation of the second metal. In order to form the shell structure, the second metal was added once the nanoparticles of the first metal were formed. The quantity of organic reagents and base was the same as that used for bimetallic systems.

Before use, the as-prepared sols were concentrated and washed with distilled water using 50 and 30 kDa Amicon Ultra filters (Millipore) to eliminate the excess PVP and other reagents dissolved in the aqueous media. Then Pd and Pd–Au colloids were impregnated onto TiO₂ by maintaining the total metal loading at 1.5 wt%, while the ratio Pd:Au was varied from 3:1 to 1:9 on a molar basis. For all samples the impregnation solvent was evaporated by thermal treatment at 120 °C. Samples were also calcined at 300 °C to study the effect of calcination on their activity. Catalyst samples are denoted as Au–TiO₂, Pd–TiO₂, and Pd_xAu_y–TiO₂, where *x* and *y* refer to the Pd:Au molar ratio in the material (i.e. Pd₁Au₁–TiO₂ indicates a TiO₂-supported sample synthesized with 1.5 wt% total metal and with a Pd:Au molar ratio of 1). The corresponding preformed nanoparticles were also studied. Table 1 compiles the composition and characteristics of the catalysts investigated in this work.

2.3. Oxidation reactions

The oxidation of 5-hydroxymethyl-2-furfural (HMF) was carried out using an autoclave (Parr Instruments) reactor with 100 mL capacity, equipped with a mechanical stirrer (0–600 rpm) and temperature and pressure gauges [38]. The reactor was charged with an aqueous solution (25 mL distilled water) containing the appropriate amount of HMF, base (NaOH), and catalyst (HMF/metal molar ratio = 100). The autoclave was purged three times with O₂ (5 bar) and then pressurized at 10 bar. Unless indicated otherwise, the temperature was increased to 70 °C and the reaction mixture was stirred at approximately 400 rpm for 4 h. The initial time (time 0) for the reaction was taken when the set point temperature was reached (after 8 min of heating). At the end of the reaction, the reactor was cooled down to room temperature and the solution was filtered. When colloids were used as catalysts, the reaction mixture was separated using 30 and 50 kDa Amicon Ultra filters (Millipore). Then 4 mL of water were added to an aliquot of the reaction solution (1 mL) before analysis with an Agilent Infinity 1260 liquid chromatograph equipped with an Aminex HPX 87-H 300 mm × 7.8 mm column using a 0.005 M H₂SO₄ solution as the mobile phase. The compound identification was achieved by calibration using reference commercial samples.

2.4. Analytical methods

XRD and HR-TEM analyses were carried on both colloids and impregnated catalysts to verify particle sizes. XRD measurements

Table 1
Structural parameters and chemical composition of Au, Pd and Pd–Au supported on TiO₂.

Catalyst	Total metal loading (wt%)	Pd (wt%)	Au (wt%)	Molar ratio Pd:Au	Surface area (m ² /g)
Pd–TiO ₂	1.5	1.5	0	–	72
Pd ₃ Au ₁ –TiO ₂	1.5	0.93	0.57	3	73
Pd ₁ Au ₁ –TiO ₂	1.5	0.53	0.97	1	78
Pd ₁ Au ₃ –TiO ₂	1.5	0.23	1.27	0.33	79
Pd ₁ Au ₆ –TiO ₂	1.5	0.12	1.38	0.16	79
Pd ₁ Au ₉ –TiO ₂	1.5	0.08	1.42	0.11	83
Au–TiO ₂	1.5	0	1.5	–	82

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