Catalysis Today 251 (2015) 96–102

Contents lists available at ScienceDirect

Catalysis Today

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

Gold nanoparticles deposited on Amberlyst-15: Metal–acid bifunctional catalyst for cellobiose conversion to gluconic acid

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ARTICLE INFO

Article history:
Received 2 August 2014
Received in revised form 26 October 2014
Accepted 5 November 2014
Available online 23 November 2014

Keywords:
Gold nanoparticles
SiO_2–Al_2O_3
Amberlyst-15
Bifunctional catalysis
Cellobiose
Gluconic acid

ABSTRACT

Gold nanoparticles were deposited on two kinds of solid acids, i.e., amorphous SiO_2–Al_2O_3 and cation-exchange resin Amberlyst-15; the resultant materials exhibited high activity as metal–acid bifunctional catalysts. SiO_2–Al_2O_3 was impregnated with a chloride-free alkaline Au(III) solution containing Na^+ and then dried. After calcination at 623 K, gold nanoparticles with diameters of 4.2 nm (measured by X-ray diffraction) were deposited at a Au loading of 1.0 wt%. By replacing the Na^+ ions with H^+ ions through ammonium ion-exchange and heating, an acidic Au/SiO_2–Al_2O_3 catalyst was obtained. In Amberlyst-15, gold nanoparticles with diameters of 7.3 nm were deposited after impregnation and drying. Subsequent ion-exchange with dilute sulfuric acid generated the acidic form of the Au/Amberlyst-15 catalyst, which showed an esterification activity equivalent to that of the original Amberlyst-15. The catalyst exhibited high activity for the direct conversion of cellobiose to gluconic acid, which requires both acid hydrolysis and oxidation. A 45% yield of gluconic acid was obtained after 24 h of reaction under ambient air at 373 K, with an apparent synergistic effect between the gold nanoparticles and acidic resin surface.

1. Introduction

It is well known that gold nanoparticles (Au NPs) supported on metal oxides are quite different from bulk gold and show excellent activity for a variety of catalytic reactions [1]. While the particle-size effect, e.g., the sharp increase of the CO oxidation rate of smaller Au NPs (less than 5 nm), is one of the most important phenomena in gold catalysts, the acid–base properties of the support materials also play a key role in many catalytic reactions. For example, we investigated the activities of several kinds of Au-NP catalysts for CO_2 hydrogenation, and discussed the activity with respect to the acid–base properties of the supports using the electronegativity of the metal cations (x_i) in the oxides as a measure of acidity [2]; we found that CO_2 conversion over the catalyst was higher when slightly acidic supports, such as TiO_2 ($x_i = 13.5$), were used and methanol selectivity was higher over catalysts supported on basic oxides, such as ZnO ($x_i = 8.0$). Gold catalysts supported on basic to weakly acidic oxides in which the x_i values are between 8 and 14, e.g., La_2O_3, ZnO, CeO_2, ZrO_2, Fe_2O_3, and TiO_2, have been extensively prepared and applied to many reactions by numerous researchers.

Deposition–precipitation (DP) is a representative preparation technique in the liquid phase for Au catalysts supported on these oxides. By this method, a hydroxochloro gold(III) species was generated from an aqueous solution of chloroauric acid neutralized with NaOH. Apparently, this anionic species did not initiate DP onto surfaces with negative zeta potentials. The DP method is thus not applicable to SiO_2, which has an isoelectric point of around two, or for more acidic materials [3]. Examples of these strongly acidic materials, i.e., so-called solid acids, are SiO_2–Al_2O_3, acidic clays, zeolites, and cation-exchange resins.

Therefore, in some publications that report the preparation of Au catalysts supported on acidic materials, other methods were employed using different gold precursors. One example, i.e., gas-phase grafting of an organogold complex, $Me_2Au(acac)$, was used for the deposition of 6–7 nm Au NPs on amorphous SiO_2–Al_2O_3 [4]. The mononuclear gold complexes in the NaY zeolite were synthesized from the same precursor [5]. The $NH_4{}^+$-exchanged USY zeolites were reacted with chloroauric acid and treated with H_2 at 773 K resulting in the formation of Au clusters with diameters of 1.8 nm [6]. Wang et al. have reported that Au NPs were loaded onto Keggin-type, insoluble polyoxometalates ($Cs_xH_{3-x}PW_{12}O_{40}$), which were strongly acidic, using the DP with urea (DPU) method [7]. Although it has been pointed out that Au NPs on relatively acidic supports like SiO_2 became relatively large (>20 nm) even using the DPU method [8], Wang et al. confirmed by TEM observation

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http://dx.doi.org/10.1016/j.cattod.2014.11.004
0920-5861/

that small Au NPs with diameters of 2.5–2.7 nm were deposited on the acidic support. Ishida and Haruta summarized the reactions catalyzed by polymer-supported Au NPs [9]. After pretreatment with NaOH, impregnation with $HAuCl_4$ and drying afforded a deposition of Au NPs on a weakly acidic cation-exchange resin [10]. This method, however, could not stabilize Au NPs on a strongly acidic cation-exchange resin with sulfonic acid terminal groups [11].

In a previous paper, we prepared Au-NP catalysts using a new preparation procedure [12]. Four types of simple metal oxides, i.e., Al_2O_3, CeO_2, TiO_2, and SiO_2, and two types of silicate, i.e., Y-type zeolite and saponite clay, were employed as supports. Deposition of fine Au NPs with average sizes between 2.3 and 5.6 nm was confirmed on all support materials, despite significant differences in their acid-base properties, when a method involving the alkaline impregnation (AI) of gold acetate was applied. By this method, a chloride-free alkaline solution of Au(III), in which the dominant species may be $[Au(OH)_4]^-$, was prepared from gold acetate. Simple impregnation of the support materials with the solution and drying, followed by heating at 423 K, washing and drying, produced the active catalysts. This preparation method avoided the negative effects of chloride, which causes gold particle growth.

In this study, Au NPs were deposited on two strongly acidic materials, i.e., SiO_2–Al_2O_3 as an amorphous mixed oxide and strongly acidic ion-exchange resin Amberlyst-15. Control of both the gold particle size and acidity of the catalyst using the method was investigated in detail. The resultant catalysts were applied for the conversion of cellobiose to gluconic acid, which required both acid hydrolysis and oxidation reactions (Scheme 1). Cellobiose is a glucose dimer linked by a β-glycosidic bond. Acid hydrolysis of cellobiose has been investigated as a model reaction for glucose formation via the hydrolysis of cellulose [13]. Since the activities of supported gold catalysts for gluconic acid production by glucose oxidation have been reported to be very high [14], a one-pot reaction consisting of two steps, i.e., hydrolysis of cellobiose and oxidation to gluconic acid, was investigated. Au NPs on carbon nanotube and insoluble heteropolyacid support materials, e.g., Au/CNT [15] and Au/$Cs_xH_{3-x}PW_{12}O_{40}$ [7] have been used as catalysts with representative reaction conditions of 418 K and 0.5 MPa oxygen pressure. In the present study, the reaction was performed under milder conditions of 373 K under ambient air.

2. Experimental

2.1. Materials

Commercial $Au(OAc)_3$ was purchased from Alfa Aesar and used without further purification. As support materials, SiO_2–Al_2O_3 (JRC-SAH-1, Japan Reference Catalyst) and Amberlyst-15 (MP Biomedicals) were obtained and used without any pretreatment. Analytical grade reagents of D-cellobiose, D-glucose, ethanol, and acetic acid were purchased and used without further purification.

2.2. Catalyst preparation

(1) Au(III) solution

Gold acetate powder (96 mg) was dispersed in 100 mL of Na_2CO_3 aqueous solution (0.1 mol/L). After refluxing the dispersion for 1 h, a colorless, transparent alkaline Au(III) solution was obtained. It was found that the sonification pretreatment, which was described in the previous paper [12], could be omitted, as excess sonification induced the precipitation of black metallic gold, which was generated by reduction in the liquid phase.

(2) Impregnation and drying

To prepare the catalyst with a nominal Au loading of 1 wt%, 1.0 g of the support material (SiO_2–Al_2O_3 powder or Amberlyst-15 beads) was impregnated with 20 mL of the above alkaline solution of gold acetate in a PFA Petri dish. The water in the dish was evaporated to dryness with heating at 313 K under mechanical mixing. For a lower Au loading, less of the alkaline Au(III) solution was used.

(3) Post-treatment of dried catalysts

For SiO_2–Al_2O_3 supported catalyst, the dried catalyst was calcined in air at 623 K for 1 h to convert all of the impregnated Au(III) species to Au NPs. Then it was washed repeatedly with water to remove excess Na^+, dried at 373 K, and the Au/SiO_2–Al_2O_3 catalyst was obtained. It was confirmed by UV–vis measurements that neither the Au(III) ion nor the Au colloid were contained in the washed water.

In the case of Au/Amberlyst-15, the support material could not be heated at 623 K because of its lack of thermal stability. Because the color originating from the Au NPs (black-purple, depending on the loading amount) was observed after impregnation and drying, further heat-treatment was not conducted. The dried catalyst was washed with water repeatedly to remove excess Na^+, and dried at room temperature to afford the Au/Amberlyst-15 catalyst.

(4) Proton exchange

Proton exchange of the catalyst was performed using sulfuric acid or ammonium nitrate. Au/SiO_2–Al_2O_3 (1 g) was ion-exchanged with 100 mL of ammonium nitrate solution (0.2 mol/L) for 2 h, washed, dried, and then heated at 573 K for 1 h to obtain the acidic form of Au/SiO_2–Al_2O_3. The acidic form of Au/Amberlyst-15 was derived by direct H^+ exchange in 40 mL of aqueous H_2SO_4 solution (0.25 mol/L) for 2 h, followed by washing and drying.

2.3. Characterization

ICP-AES analysis was performed to determine the Au content in the Au/Amberlyst-15 catalyst. To dissolve the Au NPs deposited on the surface of Amberlyst-15, the catalyst was treated with aqua regia.

TEM observation of the Au catalysts was performed using a JEOL JEM-2010 instrument at a 200 kV acceleration voltage [12]. From five different images showing different fields of view of the same sample, five regions comprising 100 particles each were selected, and the sizes of the 500 particles were measured. The number-average particle size (d_n), volume-average particle diameter (d_v), and their standard deviations (sds) were calculated from the size distribution as follows: (average) ± (sd).

Powder X-ray diffraction (XRD) measurements were performed using a diffractometer Ultima-IV (Rigaku Co., Ltd., Cu Kα radiation). Diffraction peaks of Au in the XRD profiles were fitted with pseudo-Voigt functions to determine the peak widths. The Au crystallite size was calculated from each diffraction peak by applying Scherrer's equation taking account of the instrumental line width of 0.18°. The Au size obtained by XRD measurements (d_{XRD}) was defined as the average crystallite size obtained from Au(1 1 1) and Au(2 0 0) for Au/SiO_2–Al_2O_3, and as the crystallite size from Au(1 1 1) for Au/Amberlyst-15 depending on baseline conditions from the support materials as described later. Details of the XRD profile analysis were provided in the previous paper [12].

The number of acid sites of the catalyst was determined via the back titration method: 10 mL of NaOH solution (10 mmol/L) was added to each 50 mg sample and the mixture was allowed to stand for 1 h. A fixed quantity of the supernatant was then titrated with HCl solution (5 mmol/L).