



Bifunctional gold catalysts: Relationship between preparation method and catalytic performance in tandem cellobiose valorization

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ABSTRACT

Au was supported on carbon xerogel (CX) using various techniques and tested in tandem oxidation of cellobiose to gluconic acid (combining hydrolysis and oxidation steps in one-pot) in order to establish the relationship between the physicochemical properties of these materials and their performance as bifunctional catalysts. Notably higher selectivity to gluconic acid was obtained by catalysts with larger Au particle size showing moderate TOF. The performance of Au/CX catalysts was also affected by changes in surface chemistry of CX, introduced during deposition of Au. A direct link between the catalyst modifications and the reaction pathway was established by applying a simple reaction model to compare the rate constants of the intermediate processes. The experimental and modelled results revealed that reduction with citric acid was the most suitable method of preparation of the bifunctional catalyst. This catalyst was almost inactive in conversion of glucose and gluconic acid to side products, resulting in a 4 times higher yield of the desired product as compared to its counterpart prepared by sol-immobilization method (SI). On the other hand, the presence of PVA stabilizer on the surface of the SI catalyst resulted in the preferential oxidation of alcohol over aldehyde group in glucose, leading to poor selectivity of the cascade process. The reaction kinetics was examined and the apparent activation energy of the one-pot oxidation of cellobiose to gluconic acid was determined.

1. Introduction

Biomass is the only sustainable carbon feedstock that can be used to make renewable platform chemicals and fuels [1,2], thus the development of cost effective and competitive large-scale catalytic processes for cellulose valorization is of great scientific and industrial interest. Many polysaccharides can be upgraded to useful chemicals by applying an optimized reaction cascade [2–5]. Combining multistep reactions into one-pot process significantly decreases the cost and improves the overall efficiency by allowing the direct use of biomass substrate, minimizing the energy consuming steps such as: biomass pretreatment, separation and purification of intermediates [3], as well as shortening the reaction time [6]. For example, gluconic acid, a product of the selective oxidation of glucose, has a wide range of applications in food, pharmaceutical, polymer, concrete and paper industries [7–9]. It can be obtained via one-pot tandem oxidation of cellobiose (a disaccharide comprising two β -D-glucopyranosyls connected by a β -1,4-glycosidic bond), a model compound of cellulose, with the aid of a bifunctional catalyst [3,10–15]. This type of catalyst contains two distinctive types of active sites which are able to carry out consecutive reactions,

namely: acidic sites for hydrolysis of cellobiose to glucose (first step of the reaction), which takes place mainly on the support, and metallic sites (e.g. gold nanoparticles) which catalyze glucose oxidation to gluconic acid (second step of the tandem process) [3,16]. It should be noted that gluconic acid is an intermediate product in this cascade reaction, and as such it is prone to further oxidation/degradation under reaction conditions, especially for extended reaction times. It should be noted that the cascade oxidation of cellobiose to gluconic acid can produce a wide range of side products not only from hydrolysis of cellobiose, but also oxidation, dehydration, rehydration and cracking of cellobiose, glucose and other unidentified intermediates. Therefore, the rational design of a bifunctional catalyst for this cascade process is largely concerned with the optimization of the selectivity to the desired product.

Concerning the choice of a proper support for application in bifunctional catalysts, carbon materials provide a wide array of properties which can be easily adjusted [17–20]. For example, the pore sizes and the surface area of carbon xerogels (CXs) can be readily changed by adjusting the synthesis conditions [21–24]. Moreover, their surface chemistry can be broadly modified to provide acid/base/reactant

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binding sites for various catalytic processes [19,23,25,26]. Recently, we have demonstrated that pristine CXs can effectively catalyze the selective hydrolysis of cellobiose to glucose under mild reaction conditions, and as a consequence they can be successfully applied as alternative supports in the oxidative hydrolysis of cellobiose to gluconic acid [16].

Considering the metallic sites, gold nanoparticles (Au NPs) are undoubtedly the best candidate for application in the catalytic processes involving oxidation. This is due to the peculiar characteristics of Au relative to metals of the platinum group, such as its higher resistance to oxygen poisoning [13,27–29], high catalytic activity at lower temperatures [30] and viable reusability. Moreover, a gold catalyst is a particularly good candidate for application in tandem conversion of cellobiose to gluconic acid, because it displays greater selectivity towards oxidation of primary alcohol groups as compared to formyl groups, and at the same time it is inert towards oxidation of the secondary alcohol group in glucose [31]. Moreover, Au NPs display lower activity in C–C bond scission or C=C bond isomerization in the presence of functional groups [17], which should significantly reduce the number of side reactions in this cascade process.

Many reports dealing with preparation of Au NPs on activated carbons, carbon blacks, graphite, and carbon nanotubes can be found in the literature [28,32–35]. However, it should be noted that the origin, structure and surface properties of CXs as supports are very distinct from the aforementioned carbonaceous materials, which can dominate the support adsorption properties during catalyst synthesis. In addition, the requirements for bifunctional catalysts for application in cascade process are very different from the properties necessary for one step catalytic transformations. To our best knowledge there is no previous report dealing with the preparation methods of Au NPs supported on CXs and their influence on the performance in the tandem biomass valorization. This can be the result of the fact that the preparation of nanosized gold supported on carbon materials is a difficult task, and traditional preparation methods which are successful for deposition of finely dispersed noble metals on transition metal oxides generally fail in case of gold on carbon [36].

Despite their unquestionably interesting attributes, CX supports have been only very scarcely exploited in biomass conversion in tandem reactions [16,23]. Thus, taking into consideration the promising results obtained previously by our group from the study of the role of functionalization of carbon xerogel in Au/CX catalysts [16], the present work is focused on the comparison of various methods of preparation of Au/CX and their influence on the catalyst performance in this tandem process. A link between the physicochemical properties of these catalysts and their activity in a tandem one-pot process, found here, laid the groundwork for development of a large variety of more sophisticated bifunctional catalysts for application in various biomass upgrading reactions.

2. Experimental

2.1. Preparation of support

Carbon xerogel support (CX) was prepared by polycondensation of resorcinol with formaldehyde in water [22,37]. The gelation step was carried out at 85 °C for 72 h, which was followed by step-wise drying in a laboratory oven and finally pyrolysis at 800 °C under nitrogen flow for 6 h, applying a previously optimized heating programme [38].

2.2. Gold deposition methods

All gold catalysts were prepared using $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Sigma–Aldrich, ACS reagent) as a precursor. The Au loading was fixed at 1 wt%. A pre-sieved pristine CX support with particles smaller than 100 μm was used for all catalyst preparations.

2.2.1. Sol immobilization technique (SI)

Gold was deposited via a sol immobilization technique using poly(vinyl alcohol) (PVA) as a protective agent and NaBH_4 as a reducing agent. Briefly, an aqueous solution of gold precursor (0.024 g) was dissolved in 80 mL of distilled water and added to 120 mL of 0.2 wt% solution of PVA (PVA/Au = 0.62) under vigorous stirring. After 30 min of stirring, 0.1 M NaBH_4 in distilled water (NaBH_4/Au = 5 mol/mol) was added dropwise. In the next step, 0.99 g of CX was added under vigorous stirring. Subsequently, the mixture was stirred in darkness for a maximum time of 2 weeks. In order to improve the immobilization rate, a solution of 0.1 M NaOH was added during stirring, prior to the addition of CX. The PVA stabilizer was removed from the Au NPs surface in 3 h at 350 °C under a flow of N_2 (50 cm^3/min). Finally, the catalysts were reduced following a standard reduction method in H_2 flow (50 cm^3/min) at 250 °C, with a soaking time of 2 h. Thus prepared catalyst was abbreviated SI and the catalyst prepared with the addition of NaOH was abbreviated SI_NaOH.

2.2.2. Wet-impregnation method followed by gas phase reduction (WI_H₂) or chemical reduction (WI_NaBH₄)

In this method, 0.99 g of CX was dispersed in 20 mL of distilled water. Subsequently, 5 mL of 0.024 g of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in distilled water was added dropwise to the support slurry under sonication. Then, the solvent was evaporated at 100 °C in air, followed by a standard reduction procedure, as described above. A part of the sample was chemically reduced using a solution 0.1 M NaBH_4 in distilled water (NaBH_4/Au = 5 mol/mol) at room temperature, followed by catalyst washing and drying at 100 °C in a laboratory oven. This catalyst was abbreviated WI_NaBH₄.

2.2.3. Deposition-precipitation (DP)

An aqueous solution of 500 mL containing 0.024 g of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was mixed with 0.354 g of urea and the solution was vigorously stirred for 15 min. Under continuous stirring, 0.99 g of carbon xerogel was added and the solution was thermostated at 80 °C for 2 h. Finally, the solid catalyst was washed thoroughly with distilled water and reduced by standard procedure. The sample prepared by deposition-precipitation method was abbreviated DP.

2.2.4. Citric method (CR)

In this procedure, citric acid was used both as reducing and capping agent [39]. Typically, 0.99 g of CX was dispersed in 500 mL of isopropanol under ultrasonic treatment. Subsequently, 0.024 g of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and 0.024 g of citric acid, both dissolved separately in 10 mL of isopropanol, were simultaneously added to the suspension of CX in the ultrasonic bath. After 10 min, the ultrasonication was interrupted, and the resulting dispersion was stirred at 600 rpm at room temperature for 2 h. At the end, the catalyst was filtrated, washed with copious amounts of isopropanol followed by distilled water and dried overnight at 100 °C. The sample prepared by citric reduction was abbreviated CR.

2.2.5. Double impregnation method (DIM)

DIM method is similar to the WI method, but the former contains an additional second step of impregnation with Na_2CO_3 [40]. The initial preparation was the same as in case of WI_H₂, but after addition of the gold precursor, the suspension was ultrasonicated for 1 h. Subsequently, 20 mL of 1 M aqueous solution of Na_2CO_3 (Aldrich > 99%) was added dropwise, and the solution was left under constant ultrasonic stirring for another hour, promoting gold precipitation.

2.3. Materials characterization

Transmission electron microscopy (TEM) observations were carried out using a TEM CM 20 instrument (accelerating voltage 310 and 208 kV at nominal magnification). The actual Au metal loading in the catalysts was obtained by the ICP-OES technique using a Vista RL

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