

Recent advances in selective oxidation of biomass derived platform chemicals over gold catalysts

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Abstract

Gold is without a doubt the best known metal for chemicals oxidation. The noblest of the nobles gained its place because of its resistance to overoxidation, low temperature of operation, especially in gas phase oxidation, and fairly good selectivity when required. The aim for sustainable development and the need of new technologies opens the possibility to introduce new raw materials and new catalysts formulation. That is why new horizons appear in the otherwise uncertain future of gold catalysis. The old glory becomes now a glorious alternative and this minireview gives only a small example of it.

Keywords: biomass conversion, platform chemicals, gold catalysts, gluconic acid, 2,5-furandicarboxylic acid

Introduction

The biorefinery concept dating from the end of the last century [1] is still subject of several definitions [2]. Although technologies involving biomass processing to bioproducts/bioenergy have been in operation before the establishment of the biorefinery concept, the direct synthesis of highly valuable (platform) chemicals has revolutionized the field in the last decades [3,4]. Lignocellulosic biomass is presented as the most abundant carbohydrate-rich source in our planet, being cellulose the main component (ranging 35-50 wt%) and by far the easily usable fraction since is a polymer formed by only one monosaccharide, *i.e.* glucose. The latter, usually used as model molecule, is considered one of the most important chemicals derived from biomass. Its great utility reflects on the high number of potential molecules in which glucose could convert, transformations extensively studied in the last decade [5,6].

The first studies concerning the application of gold catalysts in aerobic oxidation reactions were reported many years ago, focusing on CO oxidation and liquid phase oxidation of diols [7,8]. The low temperature CO oxidation, H₂O₂ synthesis from H₂ and O₂ [9], water gas shift [10], C-C coupling reactions [11] and conversion of carbohydrates and alcohols to corresponding aldehydes and carboxylic compounds [12,13] are some of the most successful applications of this type of catalysts. Regarding exclusively the liquid phase oxidation of organic compounds, the application list of gold catalysts is also extensive, from the oxidation of hydrocarbons through alkanes, alkenes, alcohols, polyalcohols, benzyl compounds, amines, heterocycles to any carbohydrate derived from biomass resources [14,15].

Among the existing reactions for carbohydrates conversion, the selective oxidation of plant-biomass monomers (hexoses and/or pentoses) to corresponding carboxylic acids presents a possibility to easy integration in existing technologies. The

latter presents an incremented economic interest arisen from the use of cheap and abundant raw stock. Particularly remarkable attention has been paid to the oxidation of glucose and 5-hydroxymethylfurfural (HMF), considered top building blocks in the last decade [16–18]. In both reactions, the great activity and selectivity of Pt, Pd and Au based catalysts have been demonstrated, being gold the most suitable mainly due to its higher resistance to overoxidation, reported as a cause for Pt and Pd catalyst deactivation. In an attempt to overcome catalyst deactivation, bimetallic catalysts (mostly AuPt, AuPd and AuCu systems) has been successfully employed, pointing out to an interesting synergetic effect between the metals [18,19].

This short contribution reviews the last advances in the selective oxidation of two of the most outstanding biomass derived platform molecules, *i.e.* glucose and HMF, over heterogeneous gold-based catalysts. As the activity of gold catalysts is strongly affected by its size and interaction with the support the influence of both will be discussed below.

Glucose oxidation

The oxidation of glucose' aldehydic and alcohol functions originates different added-value products mostly used in the pharmaceutical and food industries [20] but also in polymer science and medicine [21]. The aldehyde group selective oxidation (Figure 1) is one of the most explored processes as demonstrated by the high number of related publications in the last years. The latter might be attributed to the apparent simplicity of the reaction and wide applicability of the main oxidation product – gluconic acid [20], currently produced by biotechnological processes. The subsequent oxidation of gluconic acid's secondary alcohol group (C6) gives rise to glucaric acid

(see Fig. 1), used likewise in food/pharmacy industries and most importantly essential for cholesterol reduction [22] and cancer chemotherapy [23]. Nevertheless, the production of glucaric acid from biomass has been scarcely studied over gold catalysts reason why only the aerobic oxidation of glucose to gluconic acid will be undertaken in this short review.

When referring to glucose oxidation it is important to mention that the majority of studies in the last 20 years reported the use of gold catalysts in alkaline conditions, usually employed to increase the reaction rate and to avoid irreversible deactivation by metal leaching and/or reaction intermediates adsorption [24]. Despite beneficial in some extent, the use of base affects negatively the economics of the process. A neutralization step is necessary to isolate pure gluconic acid at the end of reaction and also affects gluconic acid selectivity as glucose to fructose isomerization is favored at high pH [25]. The use of base can be avoided and recent works reported excellent results over mono- and bimetallic gold-based catalysts [19,26].

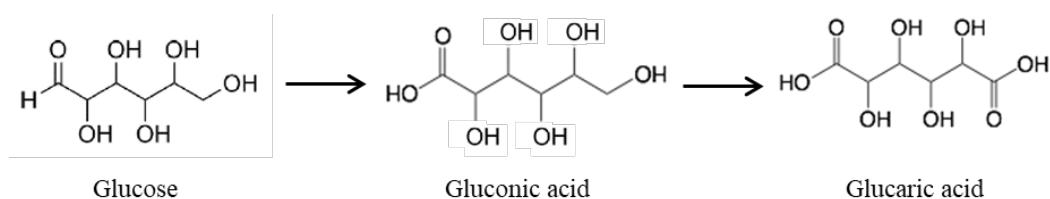


Figure 1. Subsequent oxidation of glucose to gluconic and glucaric acids.

A lot of supports have been employed in this reaction, like simple TiO_2 [27], MgO [28], ZrO_2 [29], and mixed oxides $\text{CeO}_2/\text{Al}_2\text{O}_3$ and Zn doped $\text{CeO}_2/\text{Al}_2\text{O}_3$ systems [30] and Ca – Al layered double hydroxides [31]. Our group studied the support effect

in base free conditions over a series of gold nanoparticles (3-5 nm average particle size) supported on Al_2O_3 , CeO_2 , and $\text{CeO}_2/\text{ZrO}_2$ solid solutions with different Ce/Zr molar ratio [32]. The correlation found between support's Lewis acidity and catalyst activity and selectivity reveals that the presence of more acid supports, like zirconia, promotes the formation of by-products and decreases the selectivity to the desired gluconic acid. On the other hand, the presence of reducible ceria accelerates the oxidation reaction, pointing out to a possible Mars-van Krevelen type mechanism. However, contrasting results were reported in basic conditions [33] showing presumably different oxidation pathway in presence of OH^- . In basic conditions, the oxidation of glucose is reported to proceed on Au surface via a Langmuir-Hinshelwood mechanism involving the OH^- nucleophilic attack to C1 position in glucose molecule [34]. In this way, the oxygen incorporated in the produced carboxylic acid comes presumably from the base, being the support oxygen dynamics likely not involved.

In the last years the use of carbon supports in basic free media stars gaining a lot of attention [29,35,36]. The relevance of using carbon in aqueous-phase oxidation reactions derived from its hydrophobicity and chemical stability. The former improves catalysts resistance against leaching and improves catalyst's inherent activity. As the deactivation phenomena in base-free environment is partially attributed to the metal leaching and active sites loss the use of carbon should avoid it. Related to this, an interesting and extensive recycling study over AuC catalysts has been recently reported [37]. This work evaluates the main factors of deactivation and the possible application of different reactivation procedures over the spent catalysts. Although particle agglomeration and intermediate adsorption were observed, the main deactivation cause in absence of base resulted to be gold leaching, converting all reactivation treatments

ineffective. Even though, the catalysts lost a part of their initial activity a very good recyclability with only 10% activity loss after the 4th cycle is reported.

The effect of gold particle size on the catalytic activity has been freshly studied over a series of AuC catalysts with sizes ranging 4 to 26 nm [35]. The particles size variation was controlled by a preformed colloids immobilization over activated carbon. The prepared catalysts were calcined to burn out the stabilizing agents and to elucidate the “real” size/activity effect by avoiding certain diffusional limitations during the reaction that can strongly influence the observed activity [38]. The structure/size relationship showed an optimal size around 9 nm, although after normalization to the exposed gold surface (TOF) the optimum shifted to 15-20 nm range. Benkó *et al.* found a similar trend at high pH [39] although opposite results have been also reported [40].

Nevertheless, gold particle size seems to be less influencing factor than the proper choice and modification of the support. As long as the gold particle size enters the 10-20 nm range the glucose conversion and product selectivity will depend on the nature of support, its acidity and oxygen mobility for the simple or mixed oxide supports, being the presence of ceria a key parameter. The activated carbons, on the contrary, must possess a fine balance in their hydrophobicity/hydrophilicity properties. More hydrophobic carbons avoid the gold particles leaching but also influence negatively the final gold loading during the preparation and mass transfers in aqueous phase media.

HMF oxidation

The production of 5-hydroxymethylfurfural (HMF) from lignocellulosic derivatives is one of the top studied processes in the field of biomass valorization. HMF

can be obtained via glucose isomerization to fructose and subsequent fructose dehydration, process requiring tandem Brønsted/Lewis active sites [41]. Its importance relies in the huge number of chemicals that can be obtained through its conversion among which stand out those for fuel applications and polymers industry [42]. Concretely, the total oxidation of both ring substituents leads to 2,5-furandicarboxylic acid (FDCA) classified by the US Department of Energy as one of the top 12 high-potential bio-based products [43] due to its high important future in bio-plastic production. The HMF oxidation to FDCA proceeds via two oxidation steps, the aldehyde oxidation is usually the preferred route when gold is used as catalyst forming 5-hydroxymethyl-2-furancarboxylic acid (HMFCFA) and subsequent alcohol oxidation to form 5-formyl-2-furancarboxylic acid (FFCA) and final FDCA (Figure 2). Strong basic conditions are mostly required to achieve the alcohol to carboxylic acid transformation, conditions that present a serious drawback, the HMF fast initial degradation in absence of catalyst. Therefore, highly active catalysts are vital to avoid all possible side reactions converting rapidly the HMF into FDCA [44,45].

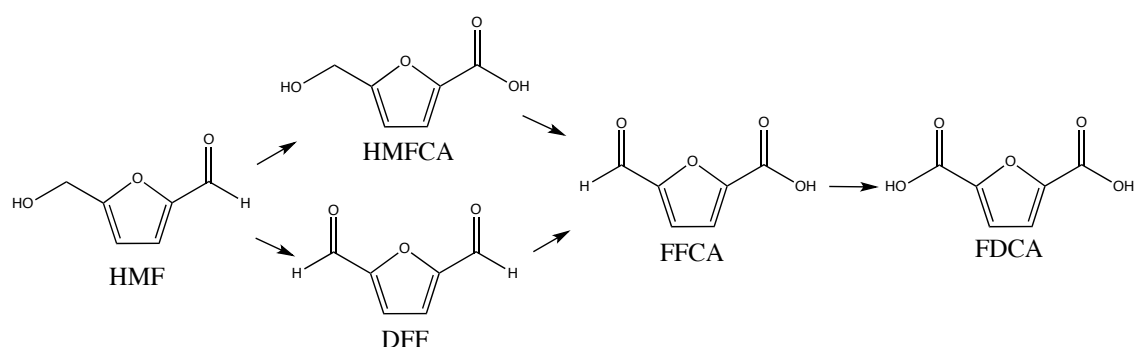


Figure 2. HMF oxidation reaction to FDCA including all possible intermediates.

For this reaction, as for glucose oxidation, the choice of support is determinant. The use of basic conditions assures the absence of gold metal leaching for the mineral

supports and many support formulations can be used. The influence of the support' Lewis/Brönsted acidity has been likewise studied in the last year over a series of Au/Ce_xZr_{1-x}O₂ catalysts with different Ce/Zr molar ratios and homogeneous gold size and shape distributions [46]. After an exhaustive low temperature CO adsorption – FTIR study, the authors found a clear trend between the surface hydroxyl Brönsted acidity and the FDCA yield in a way that higher the acid character (higher the amount of Zr⁴⁺) higher the FDCA yields. The latter was related with the already known oxidation mechanism [47] focusing in the rate-limiting HMFCA to FFCA oxidation (Figure 3). In the proposed mechanism in presence of base, the support facilitates the alkoxy intermediate formation (step b) potentiated by the presence of surface O⁻ sites (deprotonated Brönsted sites), favoring thus the FFCA formation and final FDCA yield.

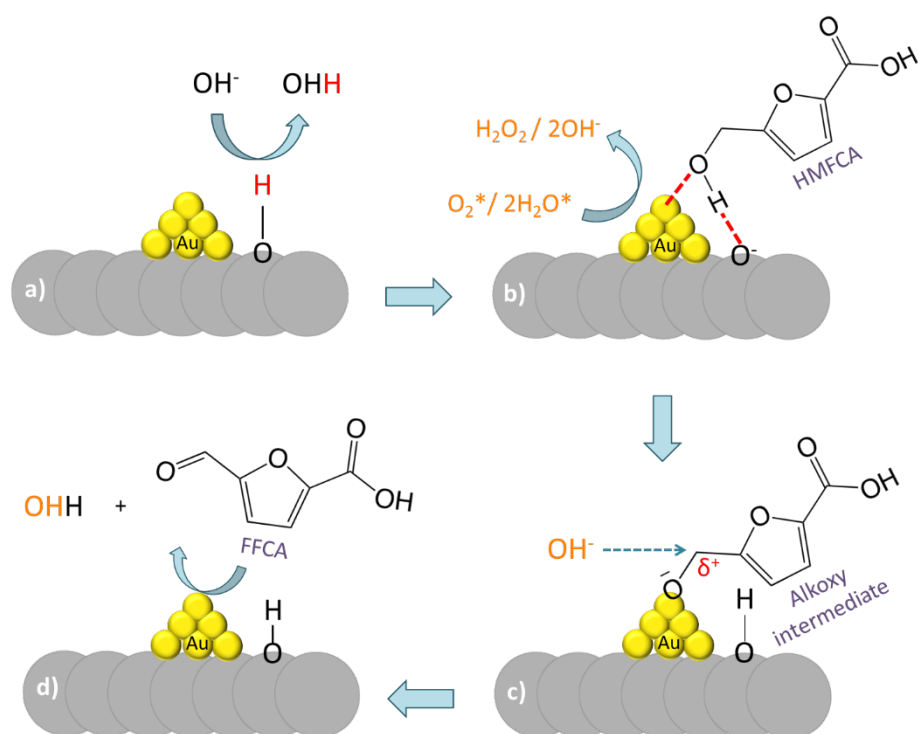


Figure 3. Proposed mechanism step for the rate-limiting step HMFCFA to FFCA reaction in basic media. Reprinted with permission from [46]. Copyright © 2018, American Chemical Society.

The particle size effect at low base concentration has been evaluated over a series of gold on carbon catalysts having 4-36 nm sizes [48]. The authors observed full HMF conversion in all cases however the products selectivity resulted to be strongly size dependent fact that was related with the Au 100/111 exposure ratio, oxygen reduction ability and base concentration. These results reveal important gold size/structure dependence in the HMFCA to FFCA oxidation at low base concentrations.

One of the newest trend in this reaction are to protect the HMF's aldehyde group before reaction in alkaline conditions [49] or to avoid the base addition during the oxidation process [50]. The former implies an additional step in the process, not preferred from industrial viewpoint but with promising results [49] thus opening a new operation route to successful exploitation of the biomass resources. On the other hand, employing strongly basic supports seems to be the key to avoid base addition during the HMF oxidation although support dissolution is now the main problem [50] difficulting the catalyst reutilization.

Concluding remarks and perspectives

Based on their incredible resistance to overoxidation the heterogeneous gold-based catalysts appeared nowadays as the best noble metal alternative for the liquid-phase oxidation of glucose and HMF under mild conditions. The less significant effect of the gold particle size on the catalytic performance in both reactions makes possible to imagine a pilot scale catalyst preparation, otherwise unviable for the gas phase oxidation reactions. From the other side a careful optimization of the physicochemical properties of the support became primordial to produce active and durable catalysts

ready to be used in large-scale biomass conversion plants. Carbonaceous materials demonstrated a clear superiority for glucose oxidation and less for HMF oxidation. However, their tunable character opens a new horizon to be explored in order to achieve a new generation of durable gold/modified-carbon catalysts for biomass conversion purposes.

Gold-based catalysts activity can be controlled also by alloying with different noble metals such as Pd, Pt and Cu. The use of bimetallic catalyst decreases the necessity to employ basic conditions. Although promising results obtained, bimetallic catalysts activity depends on a fine tuning of the intrinsic variables, *i.e.* the interaction between the metals, their relative ratio and distribution at particle' surface. The development of basic supports insensitive to pH however is presented as a competitive approach for base-free purposes.

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base during the oxidation of HMF which is the use of highly basic supports. The problems regarding the support dissolution during the reaction as well as the possible solutions to figure out this main drawback are interestingly discussed.