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Preparation of gold catalysts for glucose oxidation

Christine Baatz [*], Ulf Prüße

Institute of Technology and Biosystems Engineering, Federal Agricultural Research Centre (FAL), Bundesallee 50, 38116 Braunschweig, Germany

Abstract

The investigations focused on the influence of doping an alumina support with different base metal oxides on the catalytic performance of gold catalysts to oxidize glucose to gluconic acid. Sodium oxide and calcium oxide strongly enhanced the reaction rate for catalysts prepared by both the deposition–precipitation and incipient wetness method. Urea was used as the precipitation agent in the former. The total selectivity of the catalysts was not influenced by the dopants. TEM analysis revealed very small gold particles of less than 2 nm for sodium doped catalysts prepared by the two methods.

Keywords: Glucose oxidation; Gold catalyst; Base metal oxide doping; Deposition–precipitation with urea; Incipient wetness

1. Introduction

Since our fossil raw materials are decreasing, the chemical industry has to focus on the necessity to change over to renewable resources as a feedstock. Carbohydrates may be a good choice as a suitable major feedstock as they represent the greatest part of biomass, and have already a stereogenic framework for the synthesis of complex organic structures. In this context, the heterogeneous catalytic oxidation of low molecular weight carbohydrates like glucose is very promising as such processes can easily be integrated in already existing carbohydrate technologies. An example for a technically valuable sugar acid is the biodegradable D-gluconic acid, which can be used widely in the pharmaceutical and food industry as well as in the paper or the concrete producing industry. It is characterized by very useful complexing properties, and stability against hydrolysis at high temperatures and high pH [1]. The annual worldwide production of gluconic acid and its derivatives, so far almost exclusively prepared by biotechnological processes involving Aspergillus niger and Gluconobacter suboxydans, is about 100,000 t [2]. As shown by Biella et al. [3], gold catalysts used for glucose oxidation are 100% selective towards gluconic acid, and they are far superior to the existing Pt and Pd systems in terms of activity.

It is known that dopants which are not active for the reaction itself may alter the catalyst's activity and/or selectivity properties. For many gold catalyzed gas-phase reactions, for example, the oxidation of CO, total oxidation of hydrocarbons or the reduction of NO and N_2O, Gluhoi et al. [4,5] could show that the addition of base metal oxides can have a great influence on the catalyst performance. Since such investigations for liquid phase reactions are missing so far, we investigated the influence of the addition of base metal oxides to an alumina support on the catalyst performance in the liquid phase glucose oxidation.

Two different preparation methods, the deposition–precipitation method using urea as precipitation agent (DP urea), and the incipient wetness (IW) method were used for preparation of the catalysts. These two preparation methods were compared to each other with regard to activity in glucose oxidation, resulting gold particle size, and applicability.

2. Experimental

2.1. Catalyst preparation

Alumina Puralox SCFa-90 (Sasol, particle size 25 μm, BET surface area = 100 $m^2\ g^{-1}$, pore volume = 0.5 ml g^{-1}) was used as support. $HAuCl_4$ (50 wt% Au) was obtained from Chempur, $NaNO_3$ (p.a.) and $Ca(NO_3)_2{\cdot}4H_2O$ (p.a.) were from Merck and $La(NO_3)_3{\cdot}6H_2O$ from Fluka. The catalysts were prepared by deposition–precipitation using urea as precipitation agent and by

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* Corresponding author. Tel.: +49 531 596 4267; fax: +49 531 596 4199.
E-mail address: christine.baatz@fal.de (C. Baatz).

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incipient wetness. The amount of gold and the amount of the metal oxide dopant on the catalyst is always given as a weight fraction (wt%). All catalysts were used for glucose oxidation directly after preparation.

2.2. Doping of the support

The desired amount of the metal nitrate was dissolved in an amount of water which corresponds to the pore volume of the support. This solution was added dropwise to the support during intensive mixing until all of the liquid was assimilated by the support. The resulting precursor was dried in air overnight at 70 °C, and subsequently calcined in air at 500 °C for 14 h. The resulting doped support was stored under ambient conditions.

2.3. Deposition–precipitation

Details of the deposition–precipitation method are given in Ref. [6]. In a thermostatted reactor (80 °C), 2 g of the doped support were suspended in 100 ml of an aqueous solution of urea (0.21 mol l^{-1}) and the required amount of an aqueous solution of $HAuCl_4$ (5 g l^{-1} Au) was added. The suspension was vigorously stirred for 20 h and then cooled down to room temperature. Subsequently, the catalyst was separated by filtration through a sintered-glass filter (porosity 4) and washed with deionized water to remove residual Cl^- and Au species which were not deposited on the support. Afterwards, the resulting precursor was dried overnight at 70 °C, followed by calcination in air for 2 h at 200 °C.

2.4. Incipient wetness

The required amount of $HAuCl_4$ was dissolved in the amount of deionized water which corresponds to the pore volume of the doped support. This solution was added dropwise to the support during intensive mixing until all the liquid was assimilated by the support material. Afterwards the resulting precursor was dried overnight at 70 °C followed by reduction at 250 °C for 2 h in hydrogen diluted with nitrogen (5 vol.% H_2/95 vol.% N_2).

2.5. Catalyst characterization

TPR measurements of the catalysts were carried out in a TPR/TPD 2900 system (Micromeritics). Therefore, the catalyst precursors were heated in a gas flow of 5 vol.% H_2 in Ar with a heating rate of 10 K min^{-1} from room temperature up to 320 °C. The gold particle sizes were measured by TEM using a CM20 TWIN (LaB6), 200 kV system at the Leibniz Institute of Catalysis, Branch Berlin. The measurement of the pore volume and the BET surface area were done by gas adsorption of nitrogen using a Belsorp mini II system (Bel).

2.6. Catalytic testing

The performance of the catalyst was tested in glucose oxidation. The general testing procedure was described in detail earlier [6]. We used a starting concentration of 100 mmol l^{-1}, a reaction temperature of 40 °C and an oxygen flow of 500 ml min^{-1} at a constant pH of 9 as standard reaction parameters. All reactions were carried out until 100% conversion was reached. The selectivity was checked by HPLC. As the selectivity was $>99\%$ in all cases it was possible to calculate the activity directly from the titration curve of the resulting gluconate.

The specific activity related to the metal content of the catalyst was used to compare catalysts with different gold contents. Some catalysts showed an induction period, so the maximum activity was calculated for comparison.

3. Results and discussion

For gas-phase reactions like the CO oxidation it is known that the addition of base metal oxides has a beneficial effect of the catalytic performance of gold catalysts [4,5]. In this study, it was investigated whether there is a comparable effect in liquid phase oxidation especially in the gold catalyzed glucose oxidation, too. The used alumina support Puralox SCFa-90 supplied by Sasol is a highly pure alumina, e.g. the maximum sodium content from the production process is limited to 50 ppm. Thus, it can be assured that the effects we observed resulted from the doping process we carried out. The quoted metal oxide contents are the nominal ones. Furthermore, the metal oxide content was checked after the doping procedure but before the catalyst preparation by ICP and it revealed to agree with the intended metal oxide content. First it was checked whether there is an influence of the doping procedure on the BET surface area or the pore volume. Therefore, the surface areas and pore volumes of the undoped alumina support and a 0.3 wt% sodium oxide doped catalyst were measured by adsorption of gaseous nitrogen. The results presented in Table 1 revealed that there is no influence of the dopant on these support properties.

The gold catalysts for the glucose oxidation were prepared on the doped support material using the deposition–precipitation method using urea as precipitation agent (DP urea) and the incipient wetness method. Detailed investigations of the applications of both preparation methods for the preparation

Table 1
Comparison of surface areas, pore volumes and pore radii of undoped Puralox SCFa-90 and 0.3 wt% Na_2O doped Puralox SCFa-90

	Puralox SCFa-90 (undoped)	Puralox SCFa-90 (0.3 wt% Na_2O)
BET surface area ($m^2\,g^{-1}$)	101	100
Pore volume (ml g^{-1})	0.42	0.41
Pore radius (nm)	8.02	8.02

Table 2
Influence of base metal oxide support dopants (0.1 wt%) on the reduction temperatures of the catalyst precursors and activities of gold catalysts (0.3 wt% Au) for glucose oxidation

Doping additive	DP urea		Incipient wetness	
	Reduction temperature (°C)	Activity (mmol g^{-1} min^{-1})	Reduction temperature (°C)	Activity (mmol g^{-1} min^{-1})
None	164	711	191	578
Na_2O	160	1009	202	870
CaO	159	901	198	818
La_2O_3	171	757	195	338

of gold catalysts for glucose oxidation are reported elsewhere [6,7]. Different types of reduction were used for both preparation procedures. Using the DP urea method the catalysts were calcined in air, whereas the catalysts prepared by the incipient wetness method were reduced in a gas-phase reduction using hydrogen. This gas-phase reduction is necessary for catalysts prepared by incipient wetness because when these catalysts would be calcined in air as well large gold particles would result due to the chloride the catalysts contains. Choride present on a gold catalyst during the calcination procedure promotes mobility and agglomeration of the gold particles [8–10].

For the investigation of the influence of the doping additive on the reduction temperature, the dried catalyst precursors were investigated by TPR. Different reduction temperatures of unreduced catalysts prepared by the same preparation method would indicate differences in the interaction of the gold complexes with the support. In Table 2, the reduction temperatures and activities in glucose oxidation of the resulting catalysts were given. The gold content of the catalysts is in all cases 0.3 wt%, and the content of the doping metal oxide is 0.1 wt%. It is obvious that the addition of a base metal oxide has in no case an effect on the reduction temperatures for any of the preparation methods. The difference in the reduction temperatures between the catalysts prepared by DP urea and incipient wetness is caused by different gold species present on the precursor resulting from the preparation processes [6,7]. In the case of the DP urea method, the gold complexes which are deposited on the catalyst precursor contain mainly hydroxide and potentially some ammonia ligands but no or only little chloride [6]. The catalyst precursor resulting from the incipient wetness method contains gold complexes which are composed out of large amounts of chloride ligands and only small amounts of hydroxyl ligands [7].

Application of the catalysts in glucose oxidation showed that the activities are strongly affected by the nature of the doping metal oxide. Doping with either sodium or calcium leads to a large gain in activity of up to 50% as shown in Table 1. However, doping with lanthanum has no effect on the activity in case of the catalyst prepared by the DP urea method, or it reduces the activity for about 40% in case of the catalyst prepared by incipient wetness (Table 2).

The selectivity of the catalysts was found not to be influenced by the doping additives and was in all cases >99% towards gluconic acid. In the following, we used Puralox SCFa-90 doped with 0.3 wt% Na_2O as support, as we found this sodium oxide content to be the most beneficial when we investigated the correlation between catalyst activity and sodium oxide content [11]. When Gluhoi investigated the influence of base metal oxides on the performance of gold catalysts for gas-phase reactions [5] he found a catalyst consisting of Au supported on alumina doped with CeO_x and Li_2O being the most efficient one. For CeO_x he supposed that the oxygen adsorption is improved at the interface Au–CeO_x. He further suggested that the non-reducible alkali metal oxide Li_2O acts as a kind of structural promoter stabilising the formation of small gold particles. In the present case, an improved oxygen adsorption caused by a reducible metal oxide cannot take place. A structural promoting effect, as for Li_2O, may also be present in our case, but to confirm this assumption further studies are necessary [11].

The catalysts for the investigation of the effect of the support doping were prepared by two completely different preparation methods. The deposition–precipitation method using urea as precipitation agent is known to be a suitable method to prepare active catalysts with small gold particles for CO oxidation [12,13]. However, the incipient wetness method was long time considered to be unsuitable for the preparation of active gold catalysts [14–16] because it leads to large gold particles >10 nm which are not catalytically active. However, very recently some authors report on the preparation of active gold catalysts by the incipient wetness method but those preparation procedures contain always an additional step in which a treatment of the catalyst with bases occurs [17,18]. In fact, these preparation procedures are modified deposition–precipitation procedures. The group of Hutchings reported on the preparation of active gold catalysts for alcohol oxidation and synthesis of hydrogen peroxide by a wet impregnation procedure [19]. But even in this preparation procedure a ligand exchange between chloride and hydroxyl ions is likely because the impregnation solution was heated and this would force the hydrolysis of the tetrachloroaurate ion. In 2006, Hutchings et al. [20] reported further on active gold on carbon

Table 3
Comparison of the activities of various gold catalysts prepared on 0.3 wt% sodium oxide doped alumina by DP urea and incipient wetness

Gold loading (wt%)	DP urea Activity (mmol g^{-1} min^{-1})	Incipient-wetness Activity (mmol g^{-1} min^{-1})
0.1	1424	1400
0.3	952	1134
5	167	210

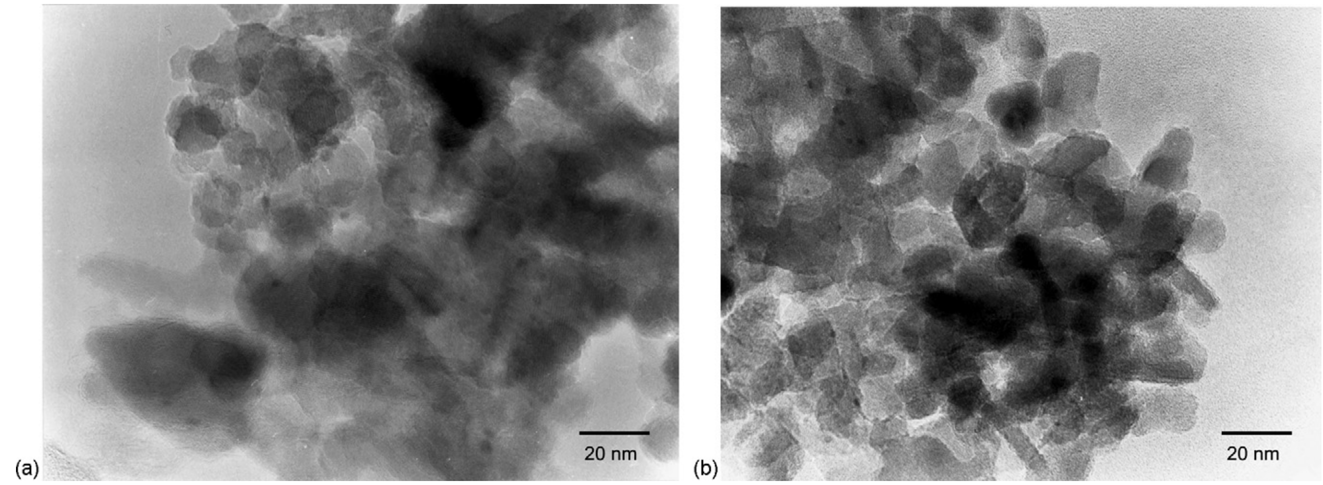

Fig. 1. TEM images of 0.3 wt% Au catalysts prepared on sodium doped alumina: (a) catalyst prepared by DP urea with gold particles of 1.4–2 nm and (b) catalyst prepared by incipient wetness with gold particles of 1.2–2 nm.

catalysts prepared by an incipient wetness method similar to the one described in this paper. Those catalysts were used in the oxidation of glycerol, cyclohexane and oxidation of primary alcohols but they are not active in CO oxidation. Unfortunately, they do not give any information about the gold particle size they achieved by using this preparation method.

In Table 3, the activities of different gold catalysts with various contents prepared on sodium oxide doped alumina by DP urea and incipient wetness are compared. It is obvious that both methods lead to very active gold catalysts over a wide range of gold loadings. In the case of the incipient wetness method it was a bit surprising that gold catalyst with a sufficient activity were obtained. The obtained activities at a certain gold loading are quite similar, so both methods are suitable for the preparation of active gold catalysts for glucose oxidation. It is noteworthy that for both methods with increasing gold content the activity decreases. For example, the catalysts with 0.1 wt% Au have activities of 1424 mmol g^{-1} min^{-1} (DP urea) and 1400 mmol g^{-1} min^{-1} (IW), respectively. Increasing the gold content up to 5% leads to a progressional decrease in activity, resulting in activities of 167 mmol g^{-1} min^{-1} (DP urea) and 210 mmol g^{-1} min^{-1} (IW). When we investigated the particle sizes of these catalysts by TEM we found a trend of increasing particle sizes with increasing gold content for both preparation methods [7]. In that study, a detailed discussion of the influence of the gold loading on the gold particle size is given. It revealed that on catalysts with higher gold loading different types of gold particles are present. On each catalyst, small gold nanoparticles with sizes between 2 and 5 nm in diameter can be found. With increasing gold content additionally other gold particles with sizes of 50 up to 200 nm can be found. These particles do not contribute to the catalytic activity as Comotti et al. [21] could show that gold particles have to be smaller than at least 10 nm to be active in glucose oxidation.

Nevertheless, both preparation methods lead to small gold particle sizes. In Fig. 1, TEM images of 0.3 wt% catalysts prepared by each method are shown. Both revealed the existence of very small gold particles of 1.4–2 nm for the catalyst prepared by DP urea, and 1.2–2 nm for the catalyst prepared by incipient wetness. These very small particles are in excellent agreement with the extraordinarily high activities of those catalysts. Thus, we could bring for the first time evidence that it is possible to prepare small and highly active gold particles by the incipient wetness method.

With regard to a technical preparation process, both methods seem to be feasible as they are not too complex. The deposition–precipitation method has the advantage of passing on hydrogen for reduction, but its main drawback is the generation of large amounts of ammoniacal waste water. Within the incipient wetness process no waste water is generated at all, which is a great benefit for economical and ecological reasons. Further on, smaller equipment and fewer process steps are needed to accomplish catalyst preparation. Thus, the incipient wetness can be regarded as a preferable method for the preparation of supported gold catalysts.

4. Conclusion

Doping of an alumina support with base metal oxides can have a large beneficial effect on the activity of gold catalysts for glucose oxidation. For sodium oxide and calcium oxide there is a strong activity-enhancing effect observable for both the deposition–precipitation using urea as precipitation agent and the incipient wetness method. For lanthanum oxide there is no influence on the catalytic activity for the catalysts prepared by deposition–precipitation, but a strong negative influence on the activity of catalysts prepared by incipient wetness.

The deposition–precipitation method using urea as a precipitation agent and the incipient wetness method are both very suitable for the preparation of active gold catalysts. Both methods lead to very active gold catalyst with very small gold particles with particle sizes smaller than 2 nm. This is very surprising in the case of the incipient wetness method which, for a long time, has been regarded as not being suitable for the preparation of active gold catalyst because only large gold particles are formed. For ecological and economic reasons the incipient wetness seems to be the preferential method for the preparation of gold catalysts on a larger scale.

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