

Preparation of gold catalysts for glucose oxidation by incipient wetness

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Abstract

The preparation of gold catalysts for liquid-phase glucose oxidation by the incipient wetness method was investigated. It could be shown that this preparation method is a good alternative to preparation with deposition–precipitation. TEM analysis revealed that it is possible to prepare small gold particles with particle size <2 nm by incipient wetness, even at high gold loadings. In glucose oxidation, the catalysts are very similar in terms of activity, selectivity and long-term stability to those prepared by deposition–precipitation with urea as the precipitation agent. From ecological and economical standpoints, the incipient wetness method has some advantages over the DP urea method.

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1. Introduction

Gold was long considered a less-useful noble metal for catalysis. In the 1970s, Bond [1,2] and Parravano [3] began to investigate the catalytic properties of gold and found that gold has excellent selectivity in hydrogenation and oxidation reactions, but very low activity compared with other noble metals, such as platinum and palladium. An essential breakthrough in the use of gold as a catalytic metal was the development of the deposition–precipitation (DP) and co-precipitation methods, both using sodium hydroxide as a precipitation agent, by Haruta et al. [4,5]. These authors showed that gold particles with particle sizes <4–5 nm exhibit very high activity in the oxidation of CO at and below ambient temperature, because only such small particles are able to adsorb small molecules like oxygen, hydrogen, or carbon monoxide, in contrast to larger ones.

Today, several preparation methods are used to generate catalysts with small and active gold particles [6–10]. The most frequently used preparation methods for metal oxide supports are the deposition–precipitation method, using either sodium hydroxide or urea as a precipitation agent, and the co-precipitation method. For gold on carbon catalysts, the preferred preparation method is the deposition of gold colloids. Impregnation

methods, which are commonly used for the preparation of other supported metal catalysts [11,12], turn out to be not useful for the preparation of gold catalysts. In the early experiments [1–3,13,14], impregnation methods were used for gold catalyst preparation, but the particle sizes obtained were very large, resulting in very low or no catalyst activity. Later, Zanella [15] and Soares [16] reported gold particle sizes of 10 nm, with some larger particles of up to 100 nm, using the incipient wetness method. Those catalysts showed no activity in CO oxidation. Recently, several groups [17,18] described a modified incipient wetness method in which the normal impregnation step with hydrogen-tetra-chloro-aurate is followed by an additional preparation step in which the impregnated catalyst is treated with a base to achieve an exchange of chloride against hydroxyl groups. Thus, this modified incipient wetness method is more similar to the deposition–precipitation methods than to the original incipient wetness method.

Most of the knowledge about gold catalysts came from experiments concerning CO oxidation, but some of the fundamental results can be brought forward to other reactions, such as the relationship between particle size and activity. Besides use in CO oxidation, gold catalysts also can be used in other reactions, including the epoxidation of propylene [19], hydrogenation reactions such as the hydrogenation of crotonaldehyde to crotylalcohol [20], and dehydrogenation reactions such as the dehydrogenation of methanol to formaldehyde [20]. In 2002,

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Biella et al. [9] reported on the use of gold catalysts in the liquid-phase oxidation of glucose to gluconic acid. They used gold colloids immobilized on carbon and found an outstanding selectivity (100%) towards gluconic acid. This high selectivity and the significantly improved activity indicated substantial progress compared with conventional catalysts containing platinum or palladium together with lead or bismuth [21,22].

D-gluconic acid is a very interesting biodegradable product with an annual production of 100,000 t worldwide, used in the pharmaceutical, food, paper, and concrete industries [23]. The entire annual demand of gluconic acid is met via biotechnological processes involving *Aspergillus niger* and *Gluconobacter suboxydans* [23], because the bismuth- and lead-promoted platinum and palladium catalysts currently available are not suitable for technical processes. Although a high selectivity (up to 97%) can be achieved, the main drawback is the strong deactivation during the reaction, often accompanied by leaching of the second metal. The gold catalysts prepared by Biella et al. [9] showed an increased selectivity of up to 100%. However, the long-term stability of the catalysts was not sufficient; the activity decreased by about 50% within only four repeated batches. Recently, Önal et al. [24] studied similarly prepared gold colloids on carbon and their kinetics in glucose oxidation. Although they reported a lower selectivity for gluconic acid, they confirmed in principle the results of Biella et al.

Recently, we studied alumina-supported gold catalysts prepared for glucose oxidation by deposition–precipitation using either sodium hydroxide (DP NaOH) or urea (DP urea) as a precipitation agent [25]. We found that both deposition–precipitation methods led to quite active and long-term stable catalysts for glucose oxidation, but noted large differences in the suitability of the preparation methods concerning the reproducibility and the loss of gold during the preparation process. It was not possible to adjust a definite gold content using the DP NaOH method, and gold losses of up to 70% during preparation were observed. The DP urea method was found to be very suitable for the preparation of gold catalysts with very definite gold content without any loss of gold.

In this work, we prepared gold catalysts by the incipient wetness method and investigated the reproducibility of the preparation procedure and the resulting activity as well as, in particular, the long-term stability in the liquid-phase glucose oxidation. Furthermore, we compared their properties with those catalysts prepared in the previous work [25]. The preparation of supported gold catalysts by the incipient wetness method would be advantageous, because it is a very simple and widely used method that can be easily scaled up to industrial dimensions [26].

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by two different deposition–precipitation methods using either sodium hydroxide and/or urea as a precipitation agent and also by the incipient wetness method. Alumina (Puralox SCFa-90, Sasol, particle size

25 μm , BET surface area 100 $\text{m}^2 \text{g}^{-1}$, pore volume 0.5 ml g^{-1} , doped with 0.3 wt% Na_2O) was used as a support, and HAuCl_4 (Chempur, 50 wt% Au) was used as the gold precursor. The amount of gold on the catalysts is always given as a weight fraction (wt%). All catalysts were used for glucose oxidation directly after preparation.

2.1.1. Deposition–precipitation

2.1.1.1. Deposition–precipitation with NaOH A 1.5-g (dry mass) sample of the support was suspended in 50 ml of deionized water, and the pH was adjusted to 7 by adding HCl (0.1 mol L^{-1}) dropwise. Then 3 ml of an aqueous solution of HAuCl_4 (5 g L^{-1} Au) was diluted with 50 ml of deionized water, and the pH was adjusted by adding NaOH (0.1 mol L^{-1}) dropwise. After the gold solution was poured into the support suspension, the pH was readjusted to 7. The resulting suspension was thermostatted at 80 °C for 2 h. After the suspension was cooled to room temperature, 10 ml of an aqueous solution of magnesium citrate (20 g L^{-1}) was added, and the mixture was stirred for an additional hour. Then the catalyst was treated further as described below.

2.1.1.2. Deposition–precipitation with urea In a thermostatted reactor (80 °C), 2 g of the support was suspended in 100 ml of an aqueous solution of urea (0.21 mol L^{-1}), and the specified amount of an aqueous solution of HAuCl_4 (5 g L^{-1} Au) was added quickly. The suspension was vigorously stirred for 20 h and then cooled to room temperature.

2.1.1.3. Further treatment After the gold precursor was deposited onto the support, all catalysts were treated in the same way: (i) separation from the preparation suspension by filtering through a sintered-glass filter (porosity 4); (ii) washing with 200 ml of deionized water to remove residual Cl^- ions and Au species that were not deposited on the support; (iii) drying overnight at 80 °C; and (iv) calcination in air at 200 °C.

2.1.2. Incipient wetness

The required amount of HAuCl_4 was dissolved in a volume of deionized water corresponding to the pore volume of the support. This solution was always freshly prepared and was added dropwise to the support during intensive mixing. At the completion of the addition, the support was slightly wet. The addition of the impregnation solution took about 15 min. Immediately afterwards, the resulting precursor was dried for 16 h at 80 °C and subsequently reduced in the gas phase using 5 vol% hydrogen in nitrogen at 250 °C for 2 h.

2.2. Catalyst characterization

The gold content of the prepared catalysts was determined by inductively coupled plasma–atom emission spectrometry (ICP-AES), using an Integra XM system (GBC). The catalysts were digested with a mixture of 1 ml HNO_3 (65%), 3 ml HCl (37%), and 5 ml HF (40%) in a microwave.

Some of the catalysts were investigated by temperature-programmed reduction (TPR) and TEM. The TPR measure-

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