Study of the character of gold nanoparticles deposited onto sputtered cerium oxide layers by deposition-precipitation method: Influence of the preparation parameters

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ABSTRACT

$Au/CeO_x/Si$ system was prepared by a combination of physical and chemical methods for application in the heterogeneous catalysis. Gold nanoparticles were loaded by the deposition-precipitation method ($HAuCl_4 \cdot 4H_2O$ used as a precursor) onto radio frequency magnetron sputtered layers of cerium oxide. The study focuses on the influence of the experimental parameters (pH of the solution, time of immersion) on the nature of gold deposit. After the preparation process, the samples were characterised by electron microscopy and X-ray photoelectron spectroscopy methods. The amount of gold loaded and its morphological parameters are discussed. We show that gold particles with high density and the mean diameter of around 4 nm are deposited from the solution with pH 7. In the case of higher value of pH, the uptake of gold significantly decreases and particles with slightly bigger mean diameter are deposited onto the substrate.

1. Introduction

During past few decades, systems of highly dispersed gold deposited on metal oxide supports have been attracting wide attention. The reason for this enormous interest lies in a unique catalytic activity of these gold-containing systems in numerous reactions, such as a low temperature CO oxidation, a selective hydrogenation, a selective reduction of NO by hydrocarbons, a 2-propanol oxidation or a water gas shift reaction [1–9].

The goal of a current research in a field of gold-based catalysts is to prepare a system with extremely dispersed and ultra-fine gold nanoparticles that will be highly active in various reactions. As regards their size, shape and distribution over a surface, a deposition method is crucial. The evaporation or the magnetron sputtering are ideal physical techniques for the deposition of small particles [10–13]. However, vacuum conditions are required for these processes and a large-scale production is often difficult. Therefore, the most widely used techniques for growing the nanoparticles are following three chemical methods: deposition-precipitation, impregnation and coprecipitation [14–17]. Haruta proposed in his legendary work [7] that the most successful way of the preparation of highly active gold containing systems is the deposition-precipitation. Using this method, gold precipitates onto the substrate in the form of nanoparticles if the material of the substrate (often in the powdered form) is immersed into the solution of $HAuCl_4 \cdot 4H_2O$ precursor and deionized water. The amount of gold loaded onto the substrate and also the particle sizes depend on a pH of the solution [7,18]. According to Haruta, the ideal pH for the precipitation is closely around the value of the isoelectric point (IEP) of the substrate. If the pH is lower than the isoelectric point,

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the surface is positively charged and the adsorption of the negatively charged $Au(OH)_xCl_{4-x}^-$ ions is quite intensive, resulting in high Au loading. But the deposited particles are too big, which lowers or entirely eliminates their reactivity. With the increasing pH, the amount of precipitating gold decreases as well as the size of the particles. In such case, highly dispersed particles with size of around 2–3 nm are loaded onto the substrate from the solution. Furthermore, the pH of the solution influences the amount of chlorine left at the substrate after the gold deposition. It was observed that the presence of residual chlorine significantly decreases the reactivity of the system and also causes agglomeration of gold particles [19,20]. The amount of residual chlorine is lower if the solution with a higher pH is used for the deposition. In addition, the samples are usually dried and calcined in air or reduced in H_2 for several hours at an elevated temperature in order to remove the chlorine residuals after the precipitation process. Therefore, not only the pH, but also other parameters such as temperature and concentration of the solution, the calcination or reduction procedures and their temperatures play an important role during the preparation of an active catalytic system.

Frequently, oxide substrates (CeO_2, TiO_2, SiO_2, Fe_2O_3, etc.) are used to enhance the catalytic performance of gold. Among them, cerium oxide is regarded as one of most efficient supports. Its ability to easily receive and supply oxygen during the oxidation and reduction processes (Oxygen storage capacity − OSC) is very important in various catalytic reactions. It was observed that the presence of gold nanoparticles leads to a higher reducibility of cerium oxide. The synergetic effects between gold and cerium oxide thereby improves catalytic activity of the whole system [21–23].

Regarding the applicability in heterogeneous catalysis, a high surface area of the catalyst is necessary for the high activity of the system. Industrial systems usually consist of powders, which fulfil these requirements very well. However, powders cannot be used in every case due to the low adhesion to the substrate. For example, the contact between the substrate and the catalyst or the precise area, where the catalyst is loaded is crucial in planar technologies using semi-conductors. An example could be the on-chip fuel cells, which is one of the hot topics of current research and development [24].

The alternative to the powder catalysts would be supported thin films. Lately, the adhesion and the precision of the deposition of thin films are markedly improved (e.g. by using the lithography and physical deposition techniques). CeO_2 films can be prepared with advantages by radio frequency (RF) magnetron sputtering, as was reported by groups of Iordanova and Matolín [25,26]. Using this method, layers of well-defined thickness and composition could be deposited onto different kinds of substrates. Such deposition technique is very promising for the preparation of the catalysts required for specific applications [24,27].

The presented study focuses on searching for ideal parameters to prepare the $Au/CeO_x/Si$ catalytic system, using a combination of the RF magnetron sputtering for cerium oxide layers and the deposition-precipitation method in order to load small gold nanoparticles onto the substrate. The influence of the preparation parameters and conditions on the final structure of the catalyst are studied and discussed.

The main difference between powders and RF sputtered films was discovered in dependence of gold deposit parameters on the pH of a precursor solution. Contrary to the powdered samples, better results were obtained in the case of the solution with lower values of pH. The RF sputtered films, studied here, could play an important role as catalytically active films covering the walls of reaction chambers or as a part of miniature voltage supplies, such as fuel cells.

2. Experimental

2.1. Catalyst preparation

A silicon wafer (Si(111), p-doped) was used as a base material. The cerium oxide films approximately 12–16 nm thick were sputtered from a CeO_2 target (2 inch diameter) onto the Si wafers (Ar pressure ~ $8 \cdot 10^{-1}$ Pa, RF power ~ 60 W, sample-target distance ~23 cm, deposition speed ~0.2 nm/min).

Gold was deposited onto the sputtered cerium oxide layer by the deposition-precipitation method. The CeO_2/Si supports were immersed into an aqueous solution of $HAuCl_4 \cdot 4H_2O$ precursor (Purity: 99%, Kishida Chemical Co., Osaka, Japan), each of them for different time (2 min, 6 min, 12 min, 18 min).

According to the literature [28], the isoelectric point of CeO_2 is 6.7–8.6. For preparing small gold nanoparticles, the pH of the solution should be higher than the isoelectric point of the substrate [7,18]. Therefore, the solutions with the pH of 7 and 10 were used for the gold deposition. The samples prepared from the solutions with different values of pH should exhibit differences also in the morphology of the gold deposit. The pH of the solutions were adjusted (with accuracy ± 1) by addition of 2 M NaOH (granular, 0.7 mm, purity: 98%, Kishida Chemical Co., Osaka, Japan) aqueous solution (similarly as in Refs. [29,30]).

The initial concentration of the gold precursor solutions was $10.4 \cdot 10^{-4}$ M in both cases. Following the immersion of the CeO_x/Si substrates, the samples were washed in deionized water and dried at ~65 °C. Subsequently, they were calcined at 300 °C for 2 h. The samples were chlorine-free after this preparation procedure, as was confirmed by XPS measurement.

The preparation parameters and the sample characteristics are listed in Table 1. The parameter 'particle size' represents a mean value of the diameters of the particles observed in SEM images using the Gwyddion software [31]. For each sample, typically 200–300 particles from several SEM images were used for the statistics. The 'density of the particles' is a number of the particles present on 1 μm^2 of the substrate and the 'Au amount' was calculated from the XPS data (the details of the calculation described further). The influence of the preparation parameters on the nature of gold deposit was followed.

2.2. Catalyst characterization

The amount of deposited gold was determined by means of XPS using the five-channel hemispherical analyser Omicron EA 125 and a dual anode (Mg/Al) X-ray source in an ultra-high vacuum (UHV) chamber with the base pressure below $2 \cdot 10^{-8}$ Pa. The X-ray photoelectron spectra were acquired using a source with the primary energy of 1486.6 eV (AlKα). The diameter of X-ray spot was several millimetres.

Table 1
Preparation conditions and characterization results for the studied $Au/CeO_x/Si$ samples.

Sample	pH	Time in solution [min]	Au particle size[a] [nm]	Density of the particles[a] $\cdot 10^2$ [No. of part·μm^{-2}]	Au amount[b] [arb.u.]
1	7	2	3.7	9.4	0.59
2	7	6	4.4	13.7	1.10
3	10	2	7.0	1.8	0.09
4	10	12	5.5	2.5	0.44
5	10	18	5.1	2.4	0.49

[a] Detected by SEM.
[b] Detected by XPS.