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Quantitative determination of residual silver distribution in nanoporous gold and its influence on structure and catalytic performance

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ABSTRACT

Large efforts have been made trying to understand the origin of the high catalytic activity of dealloyed nanoporous gold as a green catalyst for the selective promotion of chemical reactions at low temperatures. Residual silver, left in the sample after dealloying of a gold-silver alloy, has been shown to have a strong influence on the activity of the catalyst. But the question of how the silver is distributed within the porous structure has not finally been answered yet. We show by quantitative energy dispersive X-ray tomography measurements that silver forms clusters that are distributed irregularly, both on the surface and inside the ligaments building up the porous structure. Furthermore, we find that the role of the residual silver is ambiguous. Whereas CO oxidation is supported by more residual silver, methanol oxidation to methyl formate is hindered. Structural characterisation reveals larger ligaments and pores for decreasing residual silver concentration.

1. Introduction

Nanoporous gold (npAu) has attracted increasing interest over the last years especially because of its high catalytic activity [1–7], its usefulness for sensor or actuator applications [7–9] and its application in fuel cells [10]. Gold (Au) as a catalyst is particularly interesting because of its nontoxic nature, chemical stability and its ability to promote selective reactions at low temperatures [6]. NpAu can be formed either by free or by electrochemical corrosion of a gold master alloy in an acid. During this dealloying process the less noble metal (e.g. silver) is dissolved and a foam-like structure built up of ligaments and pores evolves resulting in a porous structure, which is penetrable for gases and liquids [11–13]. The npAu structure is distinguished by a high surface to volume ratio (specific surface area around 10 m^2/g) and a large fraction of low coordinated surface atoms. Although it is disadvantageous in view of the required gold mass, it has advantages as a catalyst in comparison with gold nanoparticles. These are for example a stable structure as sintering is avoided, a tuneable structure from a few nanometers to many microns, and extremely clean surfaces. Similar to Raney Nickel, nanoporous gold is a bulk nanostructured completely unsupported catalyst. Hence, it is also discussed to be a predictable catalyst reflecting the surface chemistry and reactivity of (almost) pure gold [6], in contrast to gold nanoparticles on an oxidic support. However, small fractions of less than 1 at.% residual silver (Ag) always remain in the npAu.

Several studies show that bimetallic Au-Ag nanoparticles as powder or supported by an oxide reveal an enhanced catalytic activity by a few orders of magnitude compared to bare Au for oxidation reactions using molecular oxygen (O_2) [14–16]. Also for npAu it has been shown that silver has a strong influence on its catalytic activity [4,6,16,17] as well as on the elastic properties [18]. Haruta concluded in this context that it is likely to address npAu an inversely supported gold catalyst [19]. However, the assets and drawbacks of more or less residual silver are ambiguous [4,6,17] and vary with the nature of the catalytic reaction. Furthermore, besides the fact that the catalytic performance depends on many experimental parameters such as temperature, partial pressures and acidity, the surface chemistry and hence the origin of catalytic activity can also vary depending on whether the reaction takes place in liquid or gaseous environment [20–22]. Therefore, we investigate and compare the catalytic oxidation of CO to CO_2

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in gas phase and of methanol to methyl formate in liquid phase as a function of the residual silver concentration.

To understand the role of residual silver in the performance of npAu it is important to know how the silver is spatially distributed within the porous structure. Up to now, there are only limited information [23] and speculations provided in the literature. Different studies show that ligaments with higher silver concentrations are smaller than ligaments with approximately no silver [4,18]. Further, it has been found that short dealloying times result in higher silver concentrations and that the silver concentration is not homogeneous in the nanoporous structure: a higher silver concentration in the center of a cross-section of a npAu disc of 300 μm thickness has been found compared to the concentration close to the outer surface of the disc [18]. However, a quantification of the Ag distribution within single ligaments has not been reported so far. Silver concentrations on the surfaces of gold-silver nanoparticles that are different from the average composition have been reported [15] which is also supported by different publications, in which higher metallic silver concentrations on the surface of the nanoporous gold samples compared to the average silver concentration have been found [1,17]. Haruta suggests small Ag_2O particles or patches on the surfaces of the ligaments leading to higher activities compared to the pure npAu catalyst [19]. Theoretical studies show that the presence of low coordinated surface gold atoms is essential, but not sufficient, to explain the high catalytic activity of npAu [24,25], in particular with respect to the activation of O_2. The authors suggest that chemisorbed CO interacts with atomic oxygen co-adsorbed at nearby Ag atoms. This coincides with the observation that CO prefers adsorption at low coordinated gold sites [14] whereas O_2 highly prefers adsorption on Ag [15]. In this manner, catalytic activity for CO oxidation can be enhanced by increasing the residual silver concentration providing more Ag impurities placed next to low coordinated Au surface atoms. Recently, buried silver clusters have been reported [23]. Based on kinetic Monte-Carlo simulations it has been concluded that these clusters were a relict from the dealloying process but quantification is missing and a link to catalytic results is not provided.

To explain the role of silver in the catalytic activity of npAu, electron tomography based on energy dispersive X-ray spectroscopy (EDXS) is used in order to determine how the residual Ag is distributed quantitatively in the nanoporous structure. Furthermore, we complete the characterisation of the samples by a systematic study of ligament sizes and density of low coordinated surface atoms as a function of the residual silver concentration using transmission electron microscopy (TEM). Structural and chemical characterisations have been performed at nanoporous samples before the use as a catalyst.

2. Results and discussion

2.1. Catalytic oxidation of CO and methanol

Nanoporous gold was discovered to be an active catalyst for a variety of oxidation reactions such as the oxidation of CO, d-glucose, amines and primary alcohols such as methanol and ethanol [1–7]. While the use of molecular oxygen (O_2) is preferable instead of using much harsher chemicals such as hydrogen peroxide (H_2O_2), its activation and bonding on gold type surfaces is a controversial subject [26,27]. The presence of small amounts of the less noble and more reactive Ag inside the npAu host material renders its contribution highly likely. Samples prepared with different amounts of residual silver show distinctively different catalytic activity and conversion as shown in Fig. 1. It appears that for CO oxidation with O_2 a higher fraction of Ag is beneficial resulting in a higher catalytic activity (Fig. 1a) as also reported in previous studies [7]. While for samples with Ag contents of around 1 at.% the activity is around 20 $\mu mol/(s \cdot g_{cat})$, it is increased by more than 100% for samples containing more than 10 at.% of Ag. This trend could also be observed for supported Au-Ag nanoparticle catalysts [16]. Simply, the increased fraction of Ag results in more active sites for the bonding and activation of O_2 which can react with CO adsorbed on either Au or Ag sites [24,25].

Noteworthy, a direct or linear correlation between the content of Ag and the catalytic activity cannot be drawn for the npAu catalysts. Samples with higher Ag content can also show inferior catalytic activity. As shown in Fig. 1b experiments on the aerobic oxidation of methanol in liquid phase using npAu catalysts show a strong influence of the Ag content on the conversion, here the concentration of the coupling product of methanol (methyl formate). Previous results from the gas phase catalytic oxidation of methanol already suggested that the presence of Ag may not only result in a higher activity by providing more reactive oxygen, but also foster total oxidation or build-up of inactive intermediates such as surface bonded formate [6]. Here, this trend can be confirmed also for the liquid phase oxidation reaction, where the formation of the coupling product is reduced by half when the average Ag content in the whole sample is increased from around 1 at.% to 15 at.%.

Recently, a pretreatment by ozone (O_3) was reported to result in an altered and enhanced catalytic performance for methanol oxidation in gas phase [28]. This was tested for the liquid phase oxidation by treating aliquots of one sample disc broken into several pieces either by ozone before measurement or using them in their pristine state. In general, the observed formation of the coupling product was reduced up to 30% as compared to the pristine npAu (Fig. 1b). This treatment was demonstrated to result in the oxidation and removal of hydrocarbons from the surface [29], however, it also resulted in pronounced oxidation of the Ag [30]. The considerably lower temperatures required in liquid phase oxidation (below 80 °C as compared to more than 150 °C in gas phase) may explain why this pretreatment can result in such different behaviors. In order to understand the role of Ag and its oxidized states such as Ag_2O, more detailed information on its spatial distribution are clearly required.

2.2. Measurement of residual silver distribution

The average concentration of residual silver in the whole nanoporous gold sample after dealloying as given in Fig. 1 has been determined using atomic absorption spectroscopy (AAS). With this method the total amount of silver in the npAu discs can be determined to prove that indeed samples with different residual Ag concentrations have been derived. Despite the high accuracy of this technique it only provides the total concentration of Ag in the entire sample but no information on its spatial distribution can be obtained. As shown by Hodge et al. strong concentration gradients can exist on the scale of microns along the cross-section of a npAu disc [18]. For the four samples labelled in Fig. 1 as sample A, B, C and D a more detailed characterisation is shown in Fig. 2, where evaluations of EDXS line scans in cross-sections of cleaved npAu discs are depicted. These measurements have been carried out in a scanning electron microscope (SEM). All samples show an increased Ag concentration in the center of the disc compared to the outer surface. The reason for this increase can be explained by the fact that the silver from the center of the disc has a longer way to leave the sample compared to the silver close to the surface of the disc. A further comparison of the four samples reveals that although sample D shows the highest silver concentration in the center of the disc the concentration close to the outer surface of the disc is the lowest. The AAS measurements shown in Fig. 1