

Residual silver in dealloyed nanoporous gold: quantitative spatial distribution and influence on structure and catalytic performance

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The catalytic behaviour of many chemical reactions strongly depends on the amount of residual silver left in dealloyed nanoporous gold (npAu) after corrosion of gold-silver alloys^[1]. npAu is a particularly interesting catalyst because of its non-toxic nature, its stable structure as compared to gold nanoparticles and its ability to support chemical reactions at low temperatures. It is also predestined to study the catalytic activity of almost pure gold without any (oxidic) support as it is a completely unsupported nanoporous bulk catalyst, similar to Raney-Nickel. Although the manifold influence of residual silver on the catalytic performance of npAu is known for a while, information about the quantitative spatial silver distribution is lacking.

In this contribution we present quantitative, energy dispersive X-ray spectroscopy tomography measurements of npAu^[2]. Samples have been prepared by stopping the dealloying process of gold-silver alloys (70at% Ag) in nitric acid after various times providing samples with various residual silver concentrations. For measurements in the transmission electron microscope thin, electron transparent slices or needles have been prepared using a focussed ion beam. The tomography reconstructions have been obtained with the method published by Zanaga et al.^[3] including an elemental quantification using the zeta-factor method^[4]. Our measurements show that silver is distributed irregularly within the sample. Silver rich clusters are located either buried within the material or connected to the surface of the ligaments forming the porous structure. These clusters are not present in the master alloy indicating that their formation occurs during dealloying. Some clusters show silver concentrations that are at least as large as in the master alloy. Furthermore, we show that there is a concentration gradient of silver in cross-sections of cleaved npAu discs. The silver concentration in the center of discs with a thickness of 0.25mm can be up to five times larger compared to the surface of the disc.

Also structural properties of npAu depend on the amount of residual silver. We apply a method proposed by Fujita and Chen^[5] to show that ligaments and pores are smaller if npAu contains more residual silver. Characterisation of the samples is completed by a measurement of the density of low coordinated surface atoms. As adsorption of reactive atoms or molecules is favoured at these surface sites, the catalytic activity strongly depends on this measure. We show that, although ligament and pore sizes depend on the residual silver content, the density of low coordinated surface sites is constant within the margins of error, resulting in a value that is comparable to values that can be obtained for nanoparticles^[6].

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This work was supported by the Deutsche Forschungsgemeinschaft (DFG) within the research unit FOR2213 (www.nagocat.de) and the European Research Council (ERC Starting Grant No. 335078-COLOURATOMS)