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CO oxidation on nanoporous gold: A combined TPD and XPS study of active catalysts

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ABSTRACT

Disks of nanoporous gold (np-Au), produced by leaching of silver from AgAu alloy and prepared as active catalysts for CO oxidation in a continuous-flow reactor, were investigated in detail by x-ray photoelectron spectroscopy and temperature-programmed desorption spectroscopy in ultra-high vacuum. Np-Au exhibits several oxygen species on and in the surface: Chemisorbed oxygen (O_{act}), probably generated at residual silver sites at the surface, is readily available after np-Au preparation and consumed by CO oxidation. It can be replenished on activated np-Au by exposure to O_2. In addition, strongly bound oxygen, probably at subsurface sites, is present as a major species and not consumed by CO oxidation. Pronounced CO desorption at temperatures above 200 K observed after exposing np-Au to CO at 105 K indicates an additional, more stable type of CO binding sites on np-Au as compared to pure gold. Only CO at these binding sites is consumed by oxidation reaction with O_{act}. It is proposed that the presence of strongly bound subsurface oxygen stabilizes CO adsorption on np-Au, thereby being as crucial for the observed catalytic activity of np-Au as residual silver.

1. Introduction

More than 20 years ago, the discovery of high catalytic activity of oxide-supported nanosized gold particles for CO oxidation spurred research efforts that, in the meantime, have led to prospects of profitable applications of gold as heterogeneous catalyst for gas-phase reactions, e.g., in automotive exhaust control or for selective hydrocarbon oxidation towards commodity chemicals such as propylene oxide. The fact that gold catalysts are particularly efficient for oxidation reactions at relatively low temperature came as a surprise because the noblest of all metals has, above all, a low affinity towards molecular oxygen.[2, 3] Neither molecular nor dissociative chemisorption of O_2 on planar gold surfaces, not even in the presence of steps and kinks, have been observed at temperatures from 100 to 800 K, the relevant range for catalytic activity.[4,5,6] In fact, the basic mechanism of oxygen supply in gold-catalyzed CO oxidation has been debated from the early experiments up to now.

In the case of supported gold nanoparticles, it has been proposed that adsorption and dissociation of O_2 may occur on low-coordinated gold atoms which are abundant as a consequence of the small size, or is promoted by quantum size effects[7,8,9] which render the gold nanoparticles non-metallic. Another suggestion is that O_2 dissociation involves the reducible oxide support (in particular titania) and oxygen delivery proceeds across the interface between the particle and the support.[10,11] However, meanwhile catalytic activity has also been observed for unsupported gold powder,[12] gold nanotubes embedded in polycarbonate membranes[13] and, in particular, monolithic nanoporous gold (np-Au).[14,15] Latter experiments emphasized the notion that high catalytic activity of gold for CO oxidation may require neither any support nor finely dispersed particles.

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Np-Au has a sponge-like structure, consisting of interconnected ligaments with fairly uniform diameters typically on the order of some ten nanometers. Besides CO oxidation, the material has been demonstrated to catalyze several reactions, such as selective gas-phase oxidative coupling of methanol,[16] liquid-phase oxidation of glucose,[17] electrochemical oxidation of methanol[18] and O_2 reduction in fuel cell applications.[19] Beyond that, np-Au has interesting chemo-mechanical properties and can potentially be used in sensor[20] and actuator[21] applications.

In the present study, temperature-programmed desorption (TPD) and x-ray photoemission spectroscopy (XPS) in ultra-high vacuum (UHV) were employed to gain more detailed insight into the mechanisms and surface species relevant for the catalytic performance of np-Au with respect to CO oxidation. Typically, these surface science techniques are employed at single crystal surfaces, prepared clean to act as model for the catalyst surface. In the case of gold, however, techniques that circumvent the high activation barrier of O_2 dissociation such as ozone-treatment,[22,23,24] oxygen plasma,[25,26] sputtering with oxygen ions[27,28,29,30,31] or electron-induced dissociation of a condensed layer of O_2[29] or NO_2[32] are indispensable to generate adsorbed oxygen on extended single-crystal surfaces, even when they exhibit a high density of low-coordinated sites as given in case of high-index surfaces or generated by ion bombardment.

In contrast, it is evident that in the case of np-Au there must be sustained O_2 dissociation at the surface for oxidation reactions. Experimentally, it has been proven that traces of silver as residues from the production process of np-Au are important for the catalytic activity and tune the tendency of np-Au for partial or total oxidation, implying that Ag is involved in the supply of atomic oxygen.[33,34] A recent theoretical study indeed suggested that the silver residues increase the adsorption energy of O_2 and lower its dissociation energy.[35,36] Because of the complex surface chemistry rendering the high activity for CO oxidation, we refrained from studying model systems based on single crystal gold surfaces, but employed TPD and XPS *directly* at np-Au samples which had been proven as active catalysts for CO oxidation in a continuous-flow reactor.

Investigating adsorption and reaction on porous materials by surface science techniques in UHV holds several challenges. Only the relatively small outer, i.e., visible part of the large specific surface area of the sample disks is accessible to techniques such as XPS or infrared absorption spectroscopy which provide information about chemical surface states or adsorbed species and reaction intermediates. TPD, in contrast, routinely employed to identify reaction products, may be dominated by the surface area of the inner pores. In the following, we will demonstrate that despite these challenges and despite the complexity of the material under investigation, some clear conclusions can be drawn which reveal that, besides silver, in particular various resident oxygen species on and in the surface play a role for the unique catalytic properties of np-Au. Not all of these oxygen species that interact with CO are active in such a way that they are consumed in the oxidation reaction.

2. Experimental section

Np-Au was prepared by selective electrolytic dissolution of Ag from AuAg alloy disks (30 at% Au, 70% Ag), each disk with a diameter of 4.9 mm and a thickness of 0.2 mm. The dealloying process was carried out in 5-M nitric acid at room temperature with a typical three-electrode setup. The sample (working electrode) was mounted on a gold-wire formed as a basket. The alloy disk was set to an electrochemical potential of 60 mV with respect to a Pt-foil reference electrode, a Pt foil was also deployed as counter electrode (Potentiostat, Wenking POS 88, BANK Electronics) for 32–48 hours of etching. Under the chosen conditions, 1–5 at.% Ag remain in the bulk.

The resulting material has pores and ligaments with diameters of typically 50–100 nm (see Fig. 1 for scanning electron and transmission electron micrographs (SEM, TEM) of np-Au ligaments). The specific surface area of np-Au, as determined by BET analysis of N_2 adsorption, is ~4 m^2/g from which an inner surface area of 0.1 m^2 can be calculated for a np-Au sample, i.e., ~2500 times larger than the geometric outer surface of the sample disk.

Activation of the as-prepared samples for CO oxidation was performed in a fixed-bed reactor at ambient pressure and 350 K in a continuous flow of 2 ml/min CO and 5 ml/min O_2 (using He as carrier

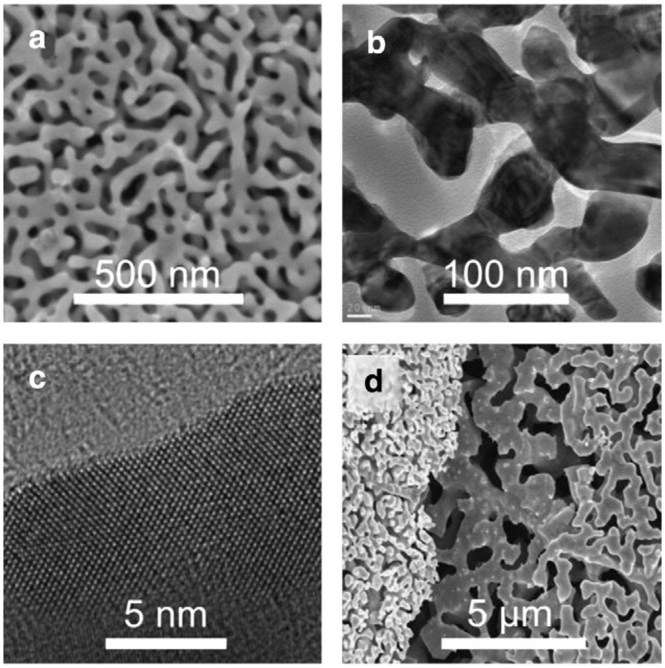

Fig. 1. a) SEM of the surface of freshly prepared, activated np-Au; b) TEM of a sample cross section produced by ultra-microtomy; c) HRTEM detail of b); d) SEM at a crack of np-Au heated to 900 K, revealing heat-induced coarsening of the ligaments.

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