



Dynamic studies of CO oxidation on nanoporous Au using a TAP reactor

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ABSTRACT

The oxidation of CO on nanoporous Au (NPG), in particular the activation of molecular O₂, was investigated by a combination of kinetic and temporal analysis of products (TAP) measurements. Continuous reaction measurements in a flow of reaction gas, at atmospheric pressure, show a catalytic behavior of the NPG, with the activity decreasing to 33% of the initial activity over 1000 min on stream. In contrast, during simultaneous pulsing of CO and O₂, the formation of CO₂ on the NPG catalyst rapidly decreased to values below the detection limit after reactive removal of the surface oxygen species present after sample preparation. Possible mechanisms explaining this discrepancy are discussed, using further information from multi-pulse TAP experiments, which revealed that molecular O₂ can be activated and stored on NPG catalyst at room temperature, though with a low probability.

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1. Introduction

Oxide-supported Au catalysts with Au nanoparticles of a few nanometers in diameter have been the subject of numerous studies since the early reports by Haruta et al. about their high activity in various oxidation and reduction reactions already at low temperatures [1,2], most prominently the CO oxidation reaction [3–5]. Despite extensive research efforts, the debate about the physical origin of their high activity as well as the underlying mechanisms still continues. While there seems to be a general consensus that apart from the Au particle size [6,7], the interaction between Au nanoparticles and oxide support plays an important role for the high activity of these Au catalysts ('interface pathway' [8,9]), other mechanisms such as reaction at undercoordinated Au sites ('Au only pathway' [9]) have been proposed and substantiated as well [10,11]. In the end, more than one reaction pathway may contribute to the reaction [12]. For the interface pathway, it is often assumed that the active sites are the perimeter sites at the interface between Au particles and oxide support and that (molecular) oxygen can be activated at these sites [9,13]. In recent quantitative measurements in a temporal analysis of products (TAP) reactor, we could indeed demonstrate that on various oxide-supported Au catalysts, active oxygen species can be reversibly stored

and reactively removed upon alternative exposure to O₂ and CO pulses [13–16]. Furthermore, for Au/TiO₂, both the oxygen storage capacity (OSC) and the reactivity of the Au/TiO₂ catalysts showed an almost linear relationship with the perimeter of the interface between Au nanoparticles and TiO₂ support, providing first direct support for the above mechanistic proposal (reaction at perimeter sites) [13].

Recently, it has been reported that monolithic nanoporous gold (NPG) prepared by leaching of Ag from an AuAg alloy also exhibits a remarkably high activity for CO oxidation [17–20]. In the absence of any support materials, it seems that interactions between metal oxide support and gold and the resulting interface sites are not mandatory for the catalytic activity of Au catalysts. On the other hand, based on the results of detailed reaction kinetic studies, Wittstock et al. suggested that the residual Ag on the surface of NPG catalysts plays a significant role in activating molecular oxygen and that these NPG catalysts should be considered as a bimetallic catalyst rather than a pure Au catalyst [18,21]. However, details of the reaction mechanism are unclear, in particular the nature of the active oxygen species and the active sites for O₂ activation.

In this paper, we report results of a combined micro-reactor and TAP reactor study on the kinetics and transient reaction behavior of the oxidation of CO over nanoporous Au catalysts. Following the description of the kinetic measurements in a micro-reactor, we present results of dynamic measurements in a TAP reactor in order to clarify whether these catalysts are also able to activate molecular oxygen and, if so, whether the amount of stored reactive oxygen (oxygen storage capacity – OSC) is correlated with the catalytic activity for CO oxidation of the respective catalysts, as it has been demonstrated for oxide-supported Au catalysts [13–16].

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2. Experimental

2.1. Nanoporous gold sample preparation

Nanoporous gold samples were prepared by electrochemical etching (dealloying) of an Ag–Au alloy, as reported previously [22,23]. The master alloy Ag₇₅Au₂₅ (at.%) was prepared by arc melting of high-purity Au and Ag wires (Au 99.9985% and Ag 99.99%, Chempur) and subsequent homogenization at 950 °C for 50 h (sealed in a quartz tube). Rectangular samples of about $1.8 \times 1 \times 1 \text{ mm}^3$ in size were cut from the ingot and annealed at 850 °C for 1.5 h under Ar for recovery. Dealloying was performed in 1 M HClO₄ aqueous solution, at a potential of 0.85 V (with respect to an Ag/AgCl reference electrode placed directly in the 1 M HClO₄ electrolyte close to the sample) for approximately one day. To minimize silver contamination in the sample compartment, the coiled-Ag wire counter electrode (CE) was separated from the main cell by placing it in a tube filled with the same solution and mounted with its opening close to the sample. The dealloying was stopped when the current fell to 10 μA . After dealloying, the electrolyte was replaced by new base electrolyte and a higher potential (0.95 V) was applied to the sample for a few hours to further remove the silver (ions) which had remained in the pore channels. Subsequently, the cell was repeatedly rinsed with fresh 1 M HClO₄ to remove traces of Ag ions in solution. The NPG disks were crushed and gently ground into powder before use.

2.2. Catalyst characterization

Since the microstructure of the NPG samples may be destroyed under the normal conditions of a BET measurement, the surface area of as-prepared NPG material was determined via the capacitance ratio method [24], yielding a value of $75 \pm 5 \text{ m}^2 \text{ g}^{-1}$. The surface morphology, microstructure and the bulk concentration of Ag were determined by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), respectively. X-ray photoelectron spectroscopy (XPS) data were recorded on a PHI 5800 ESCA system (Physical Electronics) using monochromatic Al K α radiation.

2.3. Catalytic activities measured on the flow reactor

The catalytic activity of the NPG catalyst for CO oxidation was measured in a micro-reactor with a length of 300 mm, an outer diameter of 6 mm and an inner diameter of 4 mm at atmospheric pressure at 30 °C, without applying any pretreatment prior to the measurements. One milligram of the catalyst was diluted with $\alpha\text{-Al}_2\text{O}_3$ (1:60) in order to obtain differential reaction conditions, resulting in conversions of below 15% of the reactants during the catalytic measurements. For comparison, the activity of a 3 wt.% Au/TiO₂ catalyst was also measured under the same reaction conditions. The catalyst was diluted with $\alpha\text{-Al}_2\text{O}_3$ (1:50) and pretreated by calcination in 10% O₂/N₂ at 400 °C for 30 min before reaction. The temperature of the catalyst bed is measured by a thermo couple attached to the outer wall of the reactor, centered along the catalyst bed. The flow rate of reactant gas was 60 Nml min⁻¹ (1% CO, 1% O₂, rest N₂), and both influent and effluent gases were analyzed by on-line gas chromatography (DANI, GC 86.10). For further details on the setup and the evaluation, see Ref. [25].

2.4. TAP measurements

The pulse experiments were carried out in a home-built TAP reactor [26], which is largely based on the TAP-2 approach of

Gleaves et al. [27]. In short, piezo-electric pulse valves were used to generate gas pulses of typically $\sim 1 \times 10^{16}$ molecules per pulse. For all measurements presented, these pulses contained 50% Ar as an internal standard to enable quantitative evaluation on an absolute scale. The gas pulses were directed into a quartz tube micro-reactor with a length of 90 mm, an outer diameter of 6 mm and an inner diameter of 4 mm. The catalyst bed was located in its central part and was fixed by two stainless steel sieves (Haver & Boecker OHG, transmission 25%). For all measurements, we used a three-zone catalyst bed containing 2 mg of NPG catalyst diluted with 20 mg SiO₂ as central zone and two layers of SiO₂, as outer zones (total mass 150 mg). All pulse experiments were performed at 30 °C reaction temperature. Here too, the catalyst was used as received, with no additional pretreatment prior to the measurements. After passing through the reactor, the gas pulses are analyzed by a quadrupole mass spectrometer (QMG 700, Pfeiffer) located behind the reactor tube in the analysis chamber. The consumption of CO and O₂ in the respective pulses was calculated from the missing mass spectrometric intensity in the pulses compared to the intensity after saturation, which is equivalent to the initial intensity. The formation of CO₂ could be determined directly from the CO₂ pulse intensity. The reactor can be separated from the ultrahigh vacuum (UHV) system by a differentially pumped gate valve and connected directly to an adjustable roughing pump.

In the multi-pulse experiments, the catalyst samples were exposed alternately to sequences of 200 CO/Ar and 200 O₂/Ar pulses in order to reactively remove and re-deposit active oxygen. Due to experimental reasons, the first pulse in a sequence is typically lower in intensity. For testing the catalytic activity in the TAP reactor, the samples were exposed to simultaneous pulses of CO/Ar and O₂/Ar. For both measurements, the resulting CO:O₂ ratio was 1:1 and hence there was an excess of oxygen relative to stoichiometric reaction conditions. The measurements with simultaneous pulses were used for comparison with the catalytic activity measured in the micro-reactor. In the experiments using isotope-labeled reactants, a gas mixture of ¹⁸O₂/Ar was used. Prior to these measurements, it was checked that the gas-mixing unit and the gas pipes containing the reaction mixture as well as the reactor and the dilution materials were inert, and no conversion of CO or O₂ was found under these conditions in control experiments.

To identify carbon-containing adsorbed species accumulated on the catalyst surface during reaction and oxygen species present on the surface before and after the reaction, we also performed temperature-programmed desorption (TPD) measurements in the TAP reactor. The measurements started directly after reaction, heating the catalyst from 30 °C to 600 °C with a heating rate of 25 °C min⁻¹. The gaseous desorption/decomposition products are transported by diffusion into the analysis chamber, where the effluent gases are detected by the mass spectrometer.

3. Results and discussion

As reported in references [22,28], TEM images demonstrated that the NPG material exhibits a three-dimensional nanoporous microstructure with a uniform ligament size of ca. 4 nm. The ligament size is stable in the initial oxidized state but is expected to grow after reduction. XPS characterization of the as-prepared NPG sample (see Fig. 1a) showed that the binding energy (BE) of the Au(4f_{7/2}) state is 84.4 eV, which is slightly higher than the standard BE of metallic Au (84.0 eV) [29,30]. Curve fitting of the Au(4f) signal results in a contribution of ca. 17% from an additional peak at 85.2 eV. The peak at higher BE is assigned to partially oxidized Au species [30]. The Ag(3d) XP spectrum consists of two distinct peaks at 368.4 and 374.4 eV, which are characteristic for metallic Ag⁰ [31,32], and additional smaller peaks centered at 367.8 and

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