CO oxidation on rough Au thin films grown on Si wafer

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1. Introduction

Since the discovery of the extraordinarily high catalytic activity of Au nanoparticles for reactions such as low-temperature CO oxidation, extensive studies have been devoted to the origin of this unexpected activity [1–5]. The efficiency of Au nanoparticles as heterogeneous catalysts depends on the support and therefore the role of oxide supporting materials in the enhanced catalytic activity of Au has been widely investigated [2,5]. Au nanoparticles on reducible oxides such as titania are much more catalytically active than those on non-reducible oxides [2].

It has been suggested that the oxide/Au interface is the active center of Au/oxide catalysts; for example, for CO oxidation, CO chemisorbs onto Au nanoparticles and then reacts with oxygen atoms on top of the oxide surface [2,6,7]. However, an Au-only mechanism has also been proposed, in which both CO and oxygen adsorb on Au [8–11]. Au can be partially negatively charged due to charge transfer from the oxide support, and negatively charged Au nanoparticles may be catalytically more active than neutral particles. Some experimental evidence for the negative charging of Au on active oxide supports has been reported [12]. The Au-only mechanism was further supported by experimental studies using free anionic mass-selected Au clusters [13–15].

It was recently reported that unsupported nanoporous Au exhibits significant activity for CO oxidation below room temperature; although the role of the oxide surface in enhancement of the catalytic activity of Au cannot be ruled out, the ability of Au alone to catalyze CO oxidation below room temperature has been suggested in previous studies [16–19].

In the present work, rough Au thin films containing 5% W as an impurity were prepared. CO oxidation catalyzed by these films was investigated. We demonstrate that Au thin films that cannot catalyze CO oxidation at room temperature become catalytically active at higher temperatures (>160 °C). It is likely that the W impurities enhance the stability of the Au catalyst. Using temperature-programmed desorption (TPD), the rate-determining step of CO oxidation was identified as decomposition of surface carbonate species that readily form at room temperature and desorb at higher temperatures.

2. Experimental

2.1. Preparation of rough Au films

Au films were prepared in a vacuum chamber at a base pressure of 1 × 10\textsuperscript{-2} Torr evacuated using a rotary pump. On Si wafers covered by native oxide layers, Au was evaporated by resistively heating a W wire wrapped with Au wires. During Au deposition the samples were kept at room temperature.

2.2. Reactivity and TPD measurements

The catalytic reactivity of Au films was investigated in a second chamber, as schematically illustrated in Fig. 1. The analysis chamber (base pressure 5 × 10\textsuperscript{-8} mbar) was equipped with a quadrupole mass spectrometer and a sample stage, on which samples could be heated at a constant rate using a programmed integrated differential controller. A high-pressure reactor was connected to the analysis...
chamber via a leak valve. For all reactivity measurements reported here, the initial partial pressure of O₂ and CO was 0.6 and 0.1 mbar, respectively. After the reactor was filled with CO and O₂, the change in gas composition in the reactor as a function of time was determined. A small portion of the gas was released from the reactor to the analysis chamber, where it was analyzed using the quadrupole mass spectrometer, during which the analysis chamber was backfilled to a pressure of $5 \times 10^{-7}$ mbar. The samples were clamped onto stainless plates, and a c-type thermocouple spot-welded near the sample was used for temperature measurements. The sample temperature was controlled by resistive heating of W wires spot-welded onto the sample holder.

3. Results and discussion

3.1. Surface structures of rough Au films

Fig. 2 shows scanning electron microscopy (SEM) images of Au films of different thickness. The film thickness was controlled by varying the Au evaporation time. Samples denoted as “samples 1 and 2” were further used for the reactivity experiments, whereas another with the SEM image in the middle of Fig. 2 was not further investigated. The film thickness is estimated to be approximately 10 nm for sample 1. It is evident that the mean grain size and film thickness gradually increased with increasing Au thickness. In addition to SEM, atomic force microscopy (AFM) was used for characterization of samples 1 and 2 in Fig. 2, revealing a mean particle size of $>10$ nm for sample 1 (Fig. 3).

For chemical analysis of these Au thin films, X-ray photoelectron spectroscopy (XPS) was used (Fig. 4). No Si-signal was observed, indicating that the Si surface was completely covered by Au and that the thickness of the Au film was much greater than the mean free path of the photoelectrons ($\sim 3–5$ nm) [20]. Besides Au, the presence of C, O and W was also observed in the XPS spectrum. The relative amount of W with respect to Au is estimated to be $\leq 5\%$ or less. From the chemical shift of the Au 4f level, it is evident that most of the Au was present as Au(0) (Au 4f$^{2/7}$ energy 84.1 eV). In contrast, W was mostly oxidized, as confirmed by the W 4f level shift (W 4f$^{2/7}$ energy 35.8 eV) [21]. The binding energy of the W 4f level is in agreement with the value for a WO$_3$ nanocrystalline film [22].

3.2. CO oxidation reactivity

An Au thin film with a similar surface structure to that of sample 1 in Fig. 2 was used for CO oxidation experiments. Before reactivity measurements, the sample was flashed to 300 °C and thoroughly outgassed at 160 °C. After the reactor was filled with O₂ and CO, the change in gas composition in the reactor as a function of the reaction time was determined. Fig. 5 summarizes the results of the reactivity measurements performed at a sample temperature of 160 °C. With increasing reaction time, the CO/O₂ ratio decreased, whereas the CO₂/O₂ ratio increased, implying that CO oxidation takes place. The slope of each curve at a certain point should be proportional to the temporary reaction rate (Fig. 5). When the sample stage was not sufficiently outgassed, an increase in the signal at m/z 14 signal could be observed during sample heating. An increase in the partial pressure of N₂ in the reactor should cause an increase in the peak at m/z 14 peak. Our result indicates that outgassing before reactivity measurements was effective, so that the possibility of

![Fig. 1. Schematic diagram of the experimental apparatus used for reactivity experiments.](image1)

![Fig. 2. SEM images of rough Au films grown on Si wafer. Top and side views of the films are shown. The evaporation time of each sample is indicated. In each image the scale bar corresponds to 500 nm. The samples used for the reactivity experiments are denoted as samples 1 and 2 in the figure. The sample in the middle was not used for the reactivity experiments. It is displayed to demonstrate that the grain size can be controlled by evaporation time.](image2)
significant reactor contamination by impurities during reactivity measurements can be ruled out (Fig. 5). When the reaction time exceeded ~10 h an increase in the signal at m/z 14 signal was observed, most likely due to outgassing from the reactor wall.

It is important to mention that no indication of CO oxidation could be detected at room temperature. Even when the sample was pre-annealed at 500 °C and the reaction time was increased to 10 h, no formation of CO2 could be detected for samples at room temperature. Conversion of CO to CO2 could be observed when the sample temperature was higher than 160 °C.

When the reaction temperature was increased above 200 °C, higher initial reaction rates were observed compared to those at 160 °C (Fig. 6). At a reaction temperature of 160 °C the CO2/O2 ratio increased almost linearly during measurement. In contrast, the increase in CO2/O2 ratio slowed with increasing reaction time when the reaction temperature exceeded 200 °C. At a reaction temperature of 250 °C, the CO2/O2 ratio almost saturated after

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Fig. 3. AFM images of rough Au films (samples 1 and 2 in Fig. 2) grown on Si wafer. The size of each image is 350 nm².

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Fig. 4. XPS data of a rough Au thin-film sample are displayed. (a) Si 2p region, (b) W 4d region spectrum, and (c) Au 4f region spectrum. In (a) and (b) the x-axis was magnified by a factor of 20 and 10, respectively with respect to that of (c). The amount of W is much smaller than that of Au, and Si cannot be discriminated, which should show a distinct peak at ~99 eV.
3.3. TPD results

Sample 1 was exposed to the reactant mixture (0.6 mbar O₂ and 0.1 mbar CO) at various temperatures for 10 min and TPD spectra were then collected (Fig. 8). When the sample was exposed to the reactant mixture at room temperature, CO₂ desorption was initiated when the sample temperature exceeded ~70 °C. CO₂ desorption from the sample could be observed up to a sample temperature of approximately 400 °C. CO and O₂ adsorb onto Au surfaces at room temperature; however, CO₂ desorption takes place at higher temperatures, so no reactivity can be observed at room temperature.

Haruta et al. suggested that the rate-determining step of CO oxidation catalyzed by supported Au is the decomposition of carbonate species formed on the catalyst surface [2]. In the case of Au/TiO₂, for which CO oxidation occurs at room temperature, a much lower desorption temperature was observed for CO₂ than in the present study [2]. Our result implies that the reaction mechanism for CO oxidation on rough Au thin films is analogous to that reported by Haruta et al. The higher reaction temperature for rough Au compared to the Au/TiO₂ system can be attributed to the higher binding energy of carbonate species on this surface compared to the Au/TiO₂ interface [2].

When samples were exposed to the reactant mixture at higher temperatures, the CO₂ desorption state above 250 °C became more pronounced, i.e., the formation of more strongly bound carbonate species on the surface is accelerated at higher temperature. It is most likely that these strongly bound carbonate species are...
responsible for deactivation of the catalytically active sites [26]. These TPD results are in line with the observation that deactivation of the catalytically active sites is facilitated at higher temperatures (Fig. 5). Such deactivation of Au surfaces by the formation of carbonate species has been observed for Au catalysts supported on various substrates [26].

4. Conclusions

We prepared rough Au thin films with W impurity levels of less than 5% with respect to Au. The thin films exhibited reactivity for CO oxidation at sample temperatures higher than 160 °C. The formation of carbonate species and their decomposition were suggested to be crucial for CO oxidation. However, further studies are required in order to find direct spectroscopic evidence on the carbonate formation on rough Au films. In addition, role of the W impurities for the enhancement of the catalytic activity should more systematically be studied in the future.

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