Interaction of silver with oxygen on sputtered pyrolytic graphite


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Abstract

Using core level spectra, it has been observed previously that the oxidation of silver nanoparticles deposited on sputter-damaged highly ordered pyrolytic graphite (HOPG) surfaces is very different from that taking place on surfaces composed entirely of silver. It is generally accepted that the final stage of the oxidation of silver is the formation of Ag$_2$O/AgO. However, in the case of silver nanoparticles on HOPG, Ag$_2$O/AgO can be further oxidized to give a species of unknown composition. In the present work it has been demonstrated that under these oxidizing conditions silver nanoparticles deposited on HOPG form silver carbonate. This implies that strong metal support interactions are responsible for the different behavior of silver nanoparticles on HOPG compared to that of silver in bulk. Carbonate formation is further suggested to be responsible for the deactivation of silver catalysts.

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1. Introduction

Once particles become smaller in size than about 10 nm, novel properties appear, which are not observed in larger particles of the same material. The geometric and electronic properties of nanoparticles are very different from those of the corresponding bulk material. For example, a decrease in particle size increases the relative amount of under-coordinated atoms in areas of stress such as kinks and corners, resulting in a different electronic structure [1–5]. When the particle size becomes smaller than 2–3 nm, metallic particles often undergo conductor–insulator transition [6–9].

As a consequence of the size-dependent variation in electronic and geometric properties, a corresponding change in catalytic activity may also be observed [5,6,10–14]. One of the most widely studied systems showing the size dependency of catalytic activity is gold-based heterogeneous catalysis. Gold is normally catalytically inert, but its catalytic activity is sharply enhanced once the particle size becomes smaller than about 5 nm. Other transition metals, such as silver, have similarly been found to show size dependency in heterogeneously catalyzed reactions.

Metal-support interactions must also be taken into account if the mechanism of reactions catalyzed by nanoparticles is to be understood. In the case of gold nanoparticles supported on titania or magnesia, it has been suggested that the charge transfers from the oxygen atoms of the support material to the gold nanoparticles; this forms a partially negatively charged Au atom, which is strongly active catalytically [15–19]. Where there is an even stronger metal-support interaction, atoms from the substrate may diffuse onto the nanoparticles, poisoning their catalytically active sites [20].

To shed light on the effect of particle size on the chemistry of silver, in the present study nanoparticles have been prepared on the surface of sputter-damaged highly ordered pyrolytic graphite (HOPG), as in our earlier work [21]. Samples of different mean particle size have been exposed to atomic and excited molecular oxygen environments and the oxidation behavior of the silver nanoparticles studied using X-ray photoelectron spectroscopy (XPS). The oxygen atmosphere was prepared by backfilling the vacuum chamber with
molecular oxygen in the presence of a hot platinum filament positioned close to the sample [22]. As shown in Fig. 1, different oxidation behavior was found with silver nanoparticles smaller and larger than 4 nm in diameter, respectively.

In the case of the larger silver nanoparticles, formation of silver oxides (Ag$_2$O or AgO) has been identified by the O 1s peak at 531–532 eV for Ag/HOPG could be considered to be associated with the silver rather than the HOPG support.

In the present work, our previously published XPS data on oxidized silver nanoparticles on HOPG have been analyzed in a quantitative manner [21]. In addition, valence band structures of oxidized Ag nanoparticles on sputtered HOPG have been studied using synchrotron radiation. The characteristic features of a carbonate species were observed in the valence band spectra, which also confirmed the quantitative analysis of our XPS data. It is suggested that the formation of silver carbonate is responsible for the deactivation of silver catalysts on carbon under highly oxidizing conditions.

2. Experimental

Two separate systems were used in the present work. The data in Figs. 1 and 2 and in Table 1 were produced at the University of Konstanz, Germany, whereas the remaining data were collected in the Pohang Accelerator Laboratory (beam line 7B1) in Korea.

The experimental set-up at the University of Konstanz may be briefly summarized as follows. All experiments were performed under ultra-high vacuum (UHV) conditions. XPS measurements were carried out in a UHV chamber at a base pressure of $1 \times 10^{-10}$ mbar using a cylindrical hemispherical analyzer (CHA; Omicron). A pass energy of 20 eV was used. The binding energy scale of the spectrometer was calibrated using three samples: pure silver, HOPG and gold. The Ag 3d$_{5/2}$, C 1s and Au 4f$_{7/2}$ states were found at 368.3, 284.5 and 84.0 eV, respectively (X-ray source: Al K$_\alpha$ photon energy = 1486.6 eV).

The HOPG samples prepared by the scotch-tape pilling method were inserted into the UHV system and outgassed at about 700 K for in excess of 12 h. The cleanliness of the HOPG samples was confirmed using XPS. Before deposition of silver, HOPG surfaces were mildly sputtered using an argon-ion gun to create defect sites, which are known to increase the adhesion of adsorbed metals on the surface. When the HOPG surface was not sputtered, the particle density was so low that they could hardly be detected using XPS. We have used 0.5 kV to accelerate the argon ions for sputtering.

Silver nanoparticles were grown by evaporating a rod of silver (purity 99.999%, Alfa Aesar), wrapped in tungsten wires.

Table 1

<table>
<thead>
<tr>
<th>Particle size (nm)</th>
<th>Oxidation condition</th>
<th>O 1s peak center (eV)</th>
<th>Ag:O ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 min (3.5 A)</td>
<td>531.8 ± 0.2</td>
<td>1:1.7 ± 0.3</td>
</tr>
<tr>
<td>3</td>
<td>100 min (3.5 A)</td>
<td>531.2 ± 0.2</td>
<td>1:1.0 ± 0.2</td>
</tr>
<tr>
<td>4</td>
<td>100 min (3.5 A)</td>
<td>531.2 ± 0.2</td>
<td>1:1.0 ± 0.2</td>
</tr>
<tr>
<td>5</td>
<td>190 min (3.5–3.8 A)</td>
<td>531.2 ± 0.2</td>
<td>1:0.6 ± 0.1</td>
</tr>
</tbody>
</table>

For the determination of Ag:O ratios using XPS, different cross-sections of Ag 3d state and O 1s state in the photoemission were taken into account. The platinum filament currents used for the atomic oxygen preparation are given in the parentheses. For all cases shown in this table, negative chemical shifts of 0.6–0.7 eV of the Ag 3d states were found with respect to those of the respective pure Ag particles, indicative of oxidation of Ag.
During the evaporation the HOPG samples were held at room temperature.

In the Pohang Accelerator Laboratory, the UHV system is equipped with a UV-lamp, CHA and low energy electron diffraction (LEED) system. Nominally identical methods to those at the University of Konstanz were used for sample preparation. Some differences may have occurred between the results obtained at the two different locations due to variations in sample sputtering conditions and also in sample/platinum-filament geometries used in the oxidation of silver nanoparticles. It has been confirmed that the major results regarding the oxidation behavior of silver nanoparticles obtained in Konstanz could be reproduced in Pohang. In obtaining the O 1s, Ag 3d, C 1s and valence band spectra, photon energies of 600, 430, 350 and 150 eV, respectively, were used. The energy scale was calibrated using the C 1s and Ag 3d states, similar to the experiments in the University of Konstanz.

3. Results and discussion

3.1. Quantitative analysis of O 1s and Ag 3d spectra

It is worth emphasizing that the Ag 3d state shows only negative shifts on exposure to atomic oxygen, without significant change in the peak shape, confirming the oxidation of the silver [21]. For most metals, a positive core level shift is found on oxidation, but silver is an exception, oxidation producing a negative core level shift [21]. As is shown in Table 1, the Ag:O stoichiometry approaches 2:3 when silver nanoparticles of the order of 1 nm in size are exposed to atomic/excited molecular oxygen on HOPG.

In the quantitative analysis summarized in Table 1, a background spectrum of O/HOPG was subtracted from each O/Ag/HOPG spectrum. Fig. 1 gives the data before background subtraction, and the O 1s spectra after background subtraction are shown in Fig. 2. For silver nanoparticles of mean diameter 1 nm, a 10-min exposure to oxygen is enough to give saturation of oxygen uptake. For larger particles, saturation is only reached after longer exposure [21].

It appears that silver nanoparticles of about 1 nm diameter are more readily oxidized completely than are larger silver nanoparticles. For silver nanoparticles 5 nm in diameter, one can argue that AgO or Ag2O are formed on atomic/excited molecular oxygen exposure, since the ratio of silver to oxygen is greater than unity (Table 1). However, it should be noted that the O 1s peak located at 531–532 eV is not in good agreement with Ag2O/AgO formation [23,24]. The O 1s binding energies of fully oxidized silver nanoparticles of mean diameter 5 and 1 nm are similar (531–532 eV) but are significantly different from those of Ag2O/AgO. It is therefore suggested that silver nanoparticles around 5 nm in size form a mixed structure, in which part corresponds to a novel species with a Ag:O stoichiometry of 2:3, the remainder being metallic silver, possibly with some dissolved oxygen, leading to an average Ag:O stoichiometry of less than 2:3.
It has already been seen from Fig. 1 that the O/HOPG and O/Ag/HOPG are well separated, and subtraction of the background is therefore suggested to be reliable. For Ag 3d and O 1s levels, different cross-sections for photoemission were taken into account, in which the areas of the Ag 3d and O 1s peaks were divided by the corresponding cross-sections to estimate the relative amounts of Ag and O [25].

The data used for the quantitative analysis were assembled using a photon energy of 1486.6 eV at Konstanz. It should be noted that the cross-sections of the photoemission indicated by Ertl and Kuppers were calculated assuming the same photon energy as that used in the present work [25].

In other words, it has been shown that oxidation of silver crystals in bulk results in the formation of Ag$_2$O/AgO layers [26–28]. Eventually the formation of Ag$_2$O$_3$ or Ag$_3$O$_4$ has been suggested using specific synthesis techniques; however, these compounds are metastable and volatile at room temperature. This means that the observation of such oxides of higher Ag:O stoichiometry under UHV conditions is unlikely [29–31]. It could be possible that compounds which are originally unstable might become stable as the particle size decreases, in other words the thermodynamic stability of the compound may be affected by particle size. A second possible explanation of our data might be the formation of a carbonate, Ag$_2$CO$_3$. In this the Ag:O ratio is 2:3, which in good agreement with the results in Table 1 for the smallest particles.

### 3.2. Core and valence level spectra of bare and oxidized HOPG using synchrotron radiation

The intention was to show that the formation of a carbonate species could be confirmed using valence band spectra. Firstly, a sputtered HOPG sample was exposed to an atomic/excited molecular oxygen atmosphere prepared using a hot platinum filament. This would shed light on the structural changes in the HOPG surface in this oxidizing environment.

Fig. 3 demonstrates the valence band structures of a sputtered HOPG surface before and after atomic oxygen exposure (filament current 3.5 A, P(O$_2$) = 8 x 10$^{-5}$ Torr, 70 min) Before oxygen exposure, electron density of states in the region of the Fermi level is observed, associated with the $\pi$-band of HOPG. After oxygen exposure, the electron density at the Fermi level decreases in intensity, accompanied by additional broad states below this level between 5 and 10 eV. A decrease in electron density in the region of the Fermi level indicates that carbon–carbon bonds have been broken, with formation of C–O and C=O bonds. In the C 1s level, the main peak centered at 284.5 eV does not change significantly upon oxygen exposure; however, an additional state centered at 286–287 eV appears, which can be attributed to the formation of new C–O and C=O bonds following oxygen treatment (Fig. 4), as observed previously by de la Puente et al. [32]. Note that the formation of C=O and C–O bonds accounts for the O 1s states centered at 531 and 533 eV, respectively, which have also been observed in the present work (Fig. 1).

Sputtered HOPG exposed to atomic/excited molecular oxygen shows a single peak at 532 eV, which is not in line with the corresponding data in Fig. 1c, which was obtained in a different experimental set-up (Fig. 5). This may be related to the difference in sputtering as well as to the oxidation conditions induced by dissimilar sample-filament distance and platinum filament temperature. In addition, it should be noted that different HOPG samples can show various O 1s states after exposure to atomic/excited molecular oxygen. Previously, the
O 1s state of HOPG has been found to show a single peak at 533 eV [33]. In contrast, Fig. 1 shows two different states in the O 1s spectra of sputtered HOPG exposed to oxygen, suggesting that the O 1s peaks are sensitive to sample preparation, or may in some way vary from sample to sample. The electronic and chemical properties of silver nanoparticles on carbon are not sensitive to the preparation method of the substrate, which suggests that the oxidation behavior of silver should not be greatly affected by variations in the structure of the carbon support [21,34,35].

3.3. Core and valence level spectra of oxidized silver nanoparticles on HOPG obtained using synchrotron radiation

This was designed to confirm that the key results from the oxidation of silver nanoparticles (Figs. 1 and 2) could be reproduced in experiments using different samples and experimental set-up.

Fig. 5 displays the O 1s spectra of silver nanoparticles on sputter-damaged HOPG exposed to different amounts of atomic/excited molecular oxygen. Approximately five monolayers of silver, estimated by evaporator calibration in addition to XPS data, were deposited on HOPG, corresponding to a mean particle diameter greater than about 4 nm, comparable to our earlier results [21]. After 10 min exposure to atomic/excited molecular oxygen, a shoulder at 529 eV corresponding to the Ag₂O/AgO formation was observed, accompanied by a larger peak at 531 eV. At a binding energy range above 530 eV, the O/HOPG and O/Ag signals overlap and are therefore not clearly discriminated. When the Ag/HOPG sample was exposed to a larger quantity of atomic/excited molecular oxygen, the Ag₂O/AgO peak decreased in intensity, and the peak at 531 eV was seen to shift to 532 eV and to grow further. The O 1s state centered at 532 eV from the Ag/HOPG sample was more intense than that of O/HOPG, indicating a larger oxygen uptake by Ag/HOPG than the bare sputtered HOPG. The key result obtained previously [21], that the Ag₂O/AgO is converted into a separate silver compound characterized by an O 1s state at 531–532 eV after further exposure to atomic/excited molecular oxygen, is thus confirmed.

In order to better understand the nature of the oxidized silver nanoparticle on HOPG, valence band spectra of Ag/HOPG samples were collected before and after oxygen exposure (Fig. 6). On samples of silver in bulk, the O species on or within the silver shows a peak centered at 6 eV below the Fermi level, corresponding to the O 2p orbital. The peak at 6 eV is detected for both the electrophilic and the nucleophilic oxygen species bound to silver in bulk [24]. In addition to the O 2p state at 6 eV, which is common to the Ag/O species, an additional state at about 9 eV below the Fermi level is observed after increasing exposure to atomic/excited molecular oxygen (Fig. 6).

Angle-resolved ultraviolet photoelectron spectroscopy studies have shown that carbonate species on silver surfaces can exhibit three different states (2.3, 3.6 and 8.6 eV) in the valence electronic level, which is analogous to the electronic structures of inorganic carbonates [36]. Even though the peaks at 2.3 and 3.6 eV cannot be clearly identified, probably due to the overlap of states from different oxygen species associated with silver as well as carbon in this binding energy regime, the appearance of the pronounced state at about 9 eV is in agreement with carbonate formation.

In a separate study, states between 8 and 12 eV have been assigned to the carbonate species [37]. The molecular oxygen species on silver can give similar electronic features to carbonates: the O 1s state of molecularly bound oxygen lies about 1 eV higher than that of Ag₂O [38]. Three states corresponding to the molecular orbitals of the associatively bound species appear in the valence electronic level, which are suggestive of the carbonate species [36]. One should, however, note that Ag₂O/AgO formed by exposure of silver nanoparticles to atomic/excited molecular oxygen is completely transformed to this species, identified by the O 1s state at 531–532 eV, and a peak at 9 eV below the Fermi level (Figs. 1 and 2) [21]. The complete conversion of Ag₂O/AgO to molecularly bound oxygen is not likely, and thus the formation of molecular oxygen as being responsible for the feature at 9 eV below Fermi level in the valence band can be ruled out. This suggests that silver nanoparticles on HOPG form silver carbonate on exposure to atomic/excited molecular oxygen.

By comparing the details of our core level data with those in the literature, carbonate formation for the oxidized silver nanoparticles on sputtered HOPG is strongly suggested. The presence of silver carbonate shows the Ag 3d level to be negatively shifted by about 0.7 eV with respect to metallic silver, which is confirmed in the present work [21,39].

It should be noted that the molecular oxygen species should not result in a Ag core level shift. O 1s states of the silver carbonate species were found at ~530–531 eV [39–42]. Bearing in mind that the use of a different experimental set-up could give a variability in absolute binding energy of around 0.3 eV, and also a core level shift of up to ~1 eV could result from variation in particle size, the O 1s data are considered to be in agreement with the formation of silver carbonate [21].

It is also interesting to note that if silver nanoparticles on HOPG are exposed to molecular oxygen at high pressure (1 mbar for 10 min) at 470 K, two O 1s peaks, at 529 and 531 eV, have been found by Bukhtiyarov et al. [34,35], which is in agreement with the present results. However, since only O 1s
data were indicated in the previous work, it is not entirely clear whether the oxygen species formed were similar in nature to those in the present study. In Bukhtiyarov’s work a sample temperature of 470 K was used for oxygen exposure, in order to avoid the formation of carbonate; however, bulk carbonate is not completely decomposed at 470 K, even though surface layers of carbonate may not withstand this temperature [39]. Regarding the C 1s state, silver carbonate should give a C 1s state at 429 eV, which cannot be clearly identified due its overlap with carbon bound to oxygen[39].

The appearance of the O-induced features at 6 and 9 eV is more obvious in the difference spectra, which were created by subtracting the valence band spectrum of the bare Ag/HOPG sample from that of the O/Ag/HOPG samples (Fig. 7). On bare sputtered HOPG, no distinct O induced peaks were found in the valence band spectra under the conditions employed, supporting the assertion that the 6 and 9 eV peaks were associated with silver (Fig. 7).

Summarizing the experimental results, silver nanoparticles have been shown to form silver carbonate, characterized by an O peak at 9 eV, and another oxygen species showing an O 2p state at 6 eV. Since the O 1s spectrum does not indicate the presence of Ag2O/AgO (O 1s state at ~529 eV) after exposure to large amounts of atomic/excited molecular oxygen, the O 2p state at 6 eV appearing after 70 min exposure to oxygen can be assigned to a non-oxidized species, most probably subsurface oxygen. It can be suggested that at the initial stage of the oxidation (less than 10 min oxygen exposure), the nanoparticles consist of Ag2O/AgO, silver carbonate and some subsurface dissolved oxygen. At later stages of oxidation, a mixture of silver carbonate and sub-surface dissolved oxygen forms. It must however be emphasized that the sub-surface or dissolved oxygen species show O 1s states at 531–532 eV, which cannot be distinguished from silver carbonate. Even though the presence of sub-surface/dissolved oxygen is not ruled out, we have shown that it cannot entirely account for the oxidized silver nanoparticles on HOPG, based on the changes in Ag 3d and O 1s spectra as a function of oxygen exposure, as described more in detail previously [21].

4. Conclusions

By quantitatively analyzing our previously published data, it has been concluded that a silver compound with Ag:O stoichiometry of 2:3 was formed on reacting silver nanoparticles supported on carbon with atomic/excited molecular oxygen. The suggested mixture, Ag2O/AgO, was found to be the only active species resulting from the oxidation. Further studies using photoemission spectroscopy now suggest that, silver nanoparticles on carbon form silver carbonate, and it is suggested that it is carbonate formation which is probably responsible for the deactivation of silver catalysts.

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