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<table>
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<th>The Journal of Physical Chemistry</th>
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<td>Complete List of Authors:</td>
<td>Sharp, James; University of Washington, Chemistry Yao, Yunxi; University of Washington, Chemistry Campbell, Charles; University of Washington, Chemistry</td>
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Silver Nanoparticles on Fe$_3$O$_4$(111): Energetics by Ag Adsorption Calorimetry and Structure by Surface Spectroscopies

James C. Sharp Y. X. Yao and Charles T. Campbell*

Departments of Chemistry
University of Washington
Seattle, WA 98195-1700 USA

Abstract

The heat of adsorption of Ag atoms and the growth morphology of the resulting silver particles on the Fe$_3$O$_4$(111) surface at 300 K were studied by adsorption microcalorimetry, Auger electron spectroscopy (AES) and low energy ion scattering spectroscopy (LEIS). Thin films (~6 nm thick) of Fe$_3$O$_4$(111) were grown on a Pt(111) single crystal. The changes in AES and LEIS signals versus Ag coverage during Ag vapor deposition onto Fe$_3$O$_4$(111) were indicative of Ag growing as 3D particles with a fixed density of ~4 x 10$^{12}$ particles/cm$^2$. The heat of Ag adsorption increased with Ag coverage from ~230 kJ/mol initially up to within a few percent of the heat of sublimation of bulk Ag (285 kJ/mol) by ~2 ML Ag. This corresponds to an increase in Ag atom stability (decrease in chemical potential) by ~55 kJ/mol as the Ag particle size grows from <1 to ~4 nm effective diameter on Fe$_3$O$_4$(111). The Ag(solid) / Fe$_3$O$_4$(111) adhesion energy for the 4 nm particles was estimated from the integral heat of adsorption to be 2.5±0.3 J/m$^2$. The sticking probability of Ag atoms was ~0.96 initially and increased to ~0.99 by ~1.0 ML and above.

*Corresponding Author: email = campbell@chem.washington.edu

Introduction

Nanoparticles of late transition metals dispersed across the surface of oxide support materials are the key ingredients in many heterogeneous catalysts, fuel cells, other electrocatalysts and photocatalysts, which are crucial for energy, fuel and environmental technologies and chemical processing. In such materials, the nature and strength of the chemical
bonding interactions at the interface between the metal nanoparticle and the oxide surface are very important to the material’s performance, such as its catalytic activity, selectivity and long-term stability against deactivation by sintering.\textsuperscript{1-3} The strength of the interaction for metal adsorption and adhesion onto oxide surfaces is not known for many systems, yet this determines the chemical potential of the metal atoms in the supported nanoparticles, which we showed directly correlates with their resistance to sintering and their chemical and catalytic reactivity.\textsuperscript{3}

Iron oxides are promising materials for many of these applications. In particular, late transition metal nanoparticles supported on iron oxides form the basis for new materials that are being intensively investigated for use in catalysts, fuel cells, other electrocatalysts and photocatalysts. To understand these systems, many have used a model catalyst approach, whereby nanoparticles of the late transition metal are vapor deposited onto the surface of a clean single-crystalline surface of the oxide support\textsuperscript{1-3}. This allows better control of the structure of the nanoparticles and their interface to the oxide support. Thus, to understand catalysts that use iron oxide supports, many researchers have studied metal nanoparticles supported on the magnetite Fe\textsubscript{3}O\textsubscript{4}(111) surface.\textsuperscript{4-11} For example, gold supported on Fe\textsubscript{3}O\textsubscript{4}(111) has been studied for carbon monoxide oxidation and water gas shift.\textsuperscript{11} Water gas shift has also been studied over copper on Fe\textsubscript{3}O\textsubscript{4}(111).\textsuperscript{10} Palladium on Fe\textsubscript{3}O\textsubscript{4}(111) has been studied for CO oxidation.\textsuperscript{4-6} Silver, usually supported on other oxides, is known to be a catalyst for epoxidation of olefins\textsuperscript{12,13}, partial oxidation of methanol,\textsuperscript{14} and oxidation of carbon monoxide at low temperatures.\textsuperscript{15} and references therein

In this work, we report calorimetric measurements of the heat of adsorption of Ag vapor onto a clean and well-ordered Fe\textsubscript{3}O\textsubscript{4}(111) surface, wherein the Ag particle morphology is characterized by Auger electron spectroscopy (AES), and low energy ion scattering spectroscopy (LEIS). The results are analyzed to provide the relative enthalpy and chemical potential of the Ag atoms versus Ag nanoparticle size on Fe\textsubscript{3}O\textsubscript{4}(111), and the Ag / Fe\textsubscript{3}O\textsubscript{4}(111) adhesion energy. The results are compared to similar measurements of Ag particles on MgO(100) and CeO\textsubscript{2}(111).\textsuperscript{16,17} To our knowledge, no other report exists of the heat of adsorption of any metal on any iron oxide surface. A preliminary report of some of these results has appeared.\textsuperscript{18} The morphology of Ag growth on Fe\textsubscript{3}O\textsubscript{4}(001) at 200 °C, 400 °C, and 750 °C has been study by Reflection High Energy Electron Diffraction, X-ray reflectivity and diffraction, High Resolution Transmission Electron Microscopy, and Atomic Force Microscopy.\textsuperscript{15}
Experimental

The details of the calorimetric measurement of Ag gas atom adsorption energies onto oxide supports has been presented in detail elsewhere. The calorimeter was housed in an ultrahigh vacuum chamber, with a base pressure of $\sim 2 \times 10^{-10}$ Torr (rising to $\sim 1 \times 10^{-9}$ Torr, which was mainly $\text{H}_2$, during Ag deposition). It was equipped with low energy electron diffraction (LEED), Auger electron spectroscopy (AES), low-energy ion scattering spectroscopy (LEIS), a quadrupole mass spectrometer (QMS), and a quartz crystal microbalance (QCM). AES was carried out using 1.6 keV electrons from a PHI LEED system (15-120), and a Leybold-Heraeus EA11 hemispherical energy analyzer. ISS was carried out using $\text{He}^+$ ions with 1 keV primary energy from a de-focused ion gun (Leybold-Heraeus IQE 12/38). The calorimeter consists of a pulsed metal atom beam and a pyroelectric polymer (polyvinylidenefluoride, PVDF) ribbon pressed against the back of the single crystal for heat detection. The 4-mm diameter, chopped Ag atom beam is produced from a high-temperature effusion cell. The Ag was purchased from Alfa Aesar with 99.999 % purity. The metal atom beam is chopped to provide 100 ms pulses containing $\sim 0.02$ ML of Ag atoms every two seconds. One monolayer (ML) is defined throughout as $1.42 \times 10^{15} \text{atoms/cm}^2$, which is the number of oxygen atoms exposed to the vacuum per unit area for $\text{Fe}_3\text{O}_4(111)$. The absolute beam flux is measured by using a calibrated QCM. The sticking probability is measured by a modified King–Wells method, using a line-of-sight quadrupole mass spectrometer (QMS) to measure the fraction of metal atoms which strike the surface but do not adsorb. The mass spectrometer signal was calibrated by measuring the integrated desorption signal from a known amount of Ag reflected from a hot Ta foil (1100 K to 1200 K), located at the same position as the sample and corrected for average velocity.

The typical operating temperature of the effusion cell was $\sim 1380$ K, which generated some thermal radiation that impinged on the sample and also was detected by the calorimeter. The heat signal was corrected for this by subtraction, and the heat detector was calibrated using light pulses from a He-Ne laser, as described elsewhere. The amount of light adsorbed per pulse from this He-Ne laser for pulses of fixed energy was measured and found to decrease nearly linearly with Ag coverage, from its starting value on the Ag-free $\text{Fe}_3\text{O}_4(111)$ to $69 \pm 3\%$ of its starting value by 3 ML Ag, and remain constant afterwards. By setting the final reflectivity of thick multilayer Ag to the literature value for bulk Ag of $94\%$, we estimate that the initial
reflectivity for the starting Fe$_3$O$_4$(111) thin film was $91 \pm 1\%$ using this 31% decrease in absorbed light.

To convert the calorimetrically measured internal energy changes into standard enthalpy changes at the sample temperature (300 K), the excess translational energy of the metal gas atoms at the oven temperature, above that for a 300 K Maxwell–Boltzmann distribution ($\sim 0.3 \mu$J/pulse), is subtracted, and a small pressure–volume work term (RT per mole) is added, as described elsewhere.$^{19}$ The corrected enthalpy of adsorption is thus the standard molar enthalpy of adsorption at 300 K, which at high coverage, where the atoms are adding to bulk-like sites, can be compared directly to the standard heat of sublimation of the metal. The measured heats are expressed as the enthalpy of adsorption on a “per mole of adsorbed Ag” basis by correcting for the sticking probability.

The preparation of the 1 µm-thick Pt(111) single-crystal was described previously.$^{17,20}$ The preparation of Fe$_3$O$_4$(111) thin films on Pt(111) was based on the recipe of Zscherpel et al.$^{21}$ In brief, ~1 monolayer of FeO is first grown by depositing ~1 ML of Fe on Pt(111) at 300 K and annealing for 5 minutes at 900 K in $5 \times 10^{-7}$ Torr O$_2$. Then ~20 ML of Fe is deposited in $2 \times 10^{-7}$ Torr O$_2$ at 300 K, and subsequently annealed at 800 K in $5 \times 10^{-7}$ Torr O$_2$ for 5 minutes. This led to a Fe$_3$O$_4$(111) film of ~6 nm thickness, whose composition, cleanliness and order were verified by AES and LEED.

**Results and Discussion**

**Characterization of the Fe$_3$O$_4$(111) Thin Films.** The Fe$_3$O$_4$(111) thin films were characterized by AES and LEED. The AES spectra matched spectra previously reported for Fe$_3$O$_4$(111).$^{22}$ Figure 1 shows a typical LEED pattern for the grown Fe$_3$O$_4$(111) thin film. The p(2x2) LEED image is comparable to previous reports.$^{23}$

**Sticking Probability of Ag on Fe$_3$O$_4$(111).** Figure 2 shows the sticking probability as a function of Ag coverage at 300 K. The initial sticking starts at 96% and increases to ~99% by 1.0 ML Ag coverage. The flux of the Ag atomic beam was measured by the calibrated QCM. The Ag coverage was determined by time-integrating the product of the Ag flux times the sticking probability, taking into consideration the chopped Ag beam’s “on” time. This figure is the average of three independent runs.
Morphology of Ag Islands on Fe$_3$O$_4$(111). The morphology of the growing Ag film on Fe$_3$O$_4$(111) was studied by AES and LEIS. Figure 2 shows the AES measurements for Ag on Fe$_3$O$_4$(111). The circles represent the integrated intensity of the Ag(MNN) Auger peak at 351 eV normalized to the signal from a thick, bulk-like Ag film (>30 ML). The triangles represent the integrated intensity of the oxide’s O(KVV) peak at 515 eV normalized to the signal from O(KVV) AES signal from Fe$_3$O$_4$(111) with no Ag deposited.

The dashed lines in Fig. 3 also show the theoretical intensities expected for O(KVV) and Ag(MNN) if Ag grew in a layer-by-layer fashion$^{24}$ on Fe$_3$O$_4$(111). The measured AES signals change much more slowly than in layer-by-layer growth, indicating 3D island growth. The solid lines show a fit of the data to a hemispherical cap model.$^{25,26}$ As shown in Figure 3 the hemispherical cap model fits the data well. The hemispherical cap model assumes Ag growth as 3D particles on the surface in the shape of hemispheres of fixed diameter at any given coverage, and a number density that is constant, independent of Ag coverage.$^{25}$ The model represented by solid lines uses a density of $4 \times 10^{12}$ particles/cm$^2$. The model was only fit up to the Ag coverage of 2.1 ML, because after approximately 35% of the surface area is covered by Ag islands, they can begin to overlap and the assumption that the hemispheres are isolated is no longer valid.

Figure 4 shows the growth morphology of Ag on Fe$_3$O$_4$(111) as probed using He$^+$ LEIS. The integrated intensity of the Ag peak (circles) versus Ag coverage is shown. The normalized Ag LEIS signal provides a direct measure of the fraction of the surface that is covered by Ag, since it is sensitive to only the topmost atomic layer. Thus, at any Ag coverage, the Ag coverage divided by this fractional signal is equal to the average thickness on the Ag islands, in ML. Beam damage from the ion beam was minimized by measuring only a small kinetic energy range corresponding to the Ag peak and using a small ion beam exposure for each data point. The lack of ion beam effects was proven in control experiments performed with large coverage increments, which were indistinguishable from the experiments in Figure 4. This indicates that beam damage did not impact the growth measurement within the accuracy of the LEIS experiment. Also shown is the expected curve for layer-by-layer growth (dashed line) and hemispherical cap (solid line) growth with a density of $4 \times 10^{12}$ particles per cm$^2$. As with the AES data, the growth of Ag on Fe$_3$O$_4$(111) fits the hemispherical cap model well. Previously, 3D island growth was reported for Ag growth on Fe$_3$O$_4$(001) at 200 °C.$^{15}$
Heat of Adsorption of Ag on Fe$_3$O$_4$(111). Figure 5 shows the differential heat of adsorption of Ag on Fe$_3$O$_4$(111) as a function of coverage. The curve is the average of three experimental runs. The insert shows the low coverage region (0-0.8 ML) in more detail. The pulse-to-pulse standard deviation at high Ag coverages (where the heat of adsorption was constant) was 6 kJ/mol and the experiment-to-experiment standard deviation was 16 kJ/mol (6%). To rule out possible effects on the heat of adsorption due to surface damage by electrons (from doing AES and LEED after Fe$_3$O$_4$(111) film growth), a control experiment of Ag adsorption on Fe$_3$O$_4$(111) was done without doing AES or LEED before the calorimetry experiment, and no difference was observed compared to experiments where LEED and/or AES were done after film growth.

The heat of adsorption starts at ~230 kJ/mol and rises to ~277 kJ/mol by 0.5 ML, then slowly increases to the heat of sublimation of Ag (285 kJ/mol$^{27}$) by ~2 ML. The low initial heat of adsorption shows that Ag binds more weakly (~55 kJ/mol) to the Fe$_3$O$_4$(111) surface than the surface of Ag(solid) bulk. The near unity sticking probability and the fact that Ag grows as 3D particles indicate that Ag adatoms are adsorbed in very mobile precursor state and diffuse to nucleate a new Ag cluster or find and attach to an existing Ag cluster, and only a very few desorb back into the gas. The rise in the measured heat up to the heat of sublimation by 2 ML can be attributed to the effect of particle size on the binding energy of Ag to Ag nanoparticles, similar to what we have reported for Pb, Ag, and Cu on Mg(100)$^{28,29}$ and Ag on CeO$_{2-x}$(111)$^{17}$.

Heat of Ag Atom Adsorption versus Ag Particle Size. Based on the heat of adsorption data and the Ag hemispherical particle density measured using AES and LEIS, the heat of adsorption versus particle size can be determined. To do this, we divided the best-fit Ag particle density (4 x 10$^{12}$ particles/cm$^2$) by the Ag coverage (in atoms/cm$^2$) to get the average Ag particle size (in atoms), which is easily converted to an average volume and effective diameter using the bulk Ag density and the relationship between diameter and hemisphere volume, as described previously.$^{30}$ Figure 6 shows the heat of adsorption versus average Ag particle size and number of Ag atoms already in the particle. As shown in Fig. 6, the heat of adsorption grows rapidly with particle size below 2.5 nm but, after reaching a particle diameter of ~4 nm, the heat of adsorption approaches within the noise of the data to the heat of sublimation of bulk silver solid (285 kJ/mol). This ~55 kJ/mol increase in heat of adsorption corresponds to a ~55 kJ/mol decrease in the chemical potential of Ag atoms in Ag nanoparticles supported on
Fe₃O₄(111) as their particle size increases from ~0.6 nm to 4 nm. (This assumes that entropic differences with particle size are small compared to these large enthalpic effects.) Much more dramatic changes in chemical potential with particle size were seen for Ag on MgO(100), but Ag on slightly reduced CeO₂(111) surfaces behaved quite similar to these present results on Fe₃O₄(111).³¹

The implications of these results with respect to the effect of Ag particle size on the catalytic properties for Au in relation to Ag on Fe₃O₄(111), ceria, reduced ceria and MgO(100) has been discussed elsewhere, when we gave a preliminary report of these results.¹⁸

**Adhesion Energy of Ag Solid onto Fe₃O₄(111).** Using the data in Figs. 5 and 6, the adhesion energy of 3.6 nm diameter Ag particles to Fe₃O₄(111) can be calculated to be 2.5±0.3 J/m² using the simple thermodynamic cycle previously derived.³²,³³ This result is much larger than the adhesion energy for Ag nanoparticles to MgO(100) surfaces (0.3±0.3 J/m²) and similar to that for Ag nanoparticles on CeO₂₋ₓ(111) surfaces (2.3 to 2.6 J/m²).³⁰ The value of 2.5±0.3 J/m² is statistically indistinguishable from the value for Ag to itself (i.e., twice the surface energy of pure Ag solid, 2.44 J/m²¹⁶). This indicates very strong bonding at the Ag/Fe₃O₄(111) interface. The same effects of lattice mismatch discussed regarding Ag nanoparticle binding to CeO₂₋ₓ(111) surfaces³⁰, and the resulting change in adhesion energy as Ag particle size grows, are also likely to occur for Ag on Fe₃O₄(111).

**Conclusions**

Silver atoms adsorb onto Fe₃O₄(111) with an initial heat of adsorption of ~230 kJ/mol, increasing with coverage to the heat of sublimation of bulk Ag (285 kJ/mol) by ~2 ML. This initial heat of adsorption is ~55 kJ/mol weaker than Ag bonding to bulk Ag. The sticking probability was found to be ~0.96 initially and increase to ~0.99 by ~1.0 ML. Based on AES and LEIS data, Ag grows as 3D islands on Fe₃O₄(111) with a fixed particle density of 4 x 10¹² particles/cm². Using this particle density, the average size of Ag particles was calculated at each Ag coverage, and the heat of adsorption versus Ag particle size was determined. From this, it was found that the Ag atoms in Ag nanoparticles supported on Fe₃O₄(111) increase in stability (decrease in chemical potential) by ~55 kJ/mol as the Ag particle size grows from ~0.6 nm to ~4 nm, but stabilizes near the chemical potential in bulk Ag solid after reaching a diameter of ~4
nm. The adhesion energy for ~4 nm Ag(solid) particles to Fe₃O₄(111) was found to be 2.5±0.3 J/m², similar to values found for Ag on CeO₂-x(111) surfaces.

Acknowledgements

The authors acknowledge the Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division under Grant No. DE-FG02-96ER14630, for support of this work.

References


Figure 1. LEED Pattern at 60 eV of 6 nm thick Fe$_3$O$_4$(111) film grown on Pt(111). The (0,0) spot is near the center but hidden by the sample holder.

Figure 2. Sticking probability of Ag atoms onto the Fe$_3$O$_4$(111) thin film at 300 K as function of Ag coverage. One monolayer is defined as 1.42 x 10$^{15}$ atoms per cm$^2$, which is the number of oxygen atoms exposed to the vacuum per unit area for Fe$_3$O$_4$(111). The insert shows a structural model of the Fe$_3$O$_4$(111) surface.
Figure 3. Integrated Ag (circles) and O (triangles) AES intensities, normalized to bulk Ag and the clean Fe₃O₄(111) surface, respectively, versus Ag coverage at 300 K. The dashed curves correspond to the expected behavior if Ag grew layer-by-layer. The solid curves correspond to the calculated curve for a hemispherical cap model (with a Ag particle density of $4 \times 10^{12}$ particles per cm$^2$). The inelastic mean path used was 0.71 nm for Ag and 0.93 nm for O$^{34}$ and the detection angle was 45º.

Figure 4. Integrated Ag LEIS intensity, normalized to bulk Ag, versus Ag coverage at 300 K on Fe₃O₄(111). The dashed lines correspond to the expected curve if Ag grew layer-by-layer. The solid curve corresponds to the calculated curve for a hemispherical cap model (with a Ag particle density of $4 \times 10^{12}$ particles per cm$^2$).
Figure 5. Heat of Ag atom adsorption versus Ag coverage at 300 K on Fe$_3$O$_4$(111). The data is the average of three experiments. Each data point represents a pulse of 0.025 ML of Ag. The inserts shows the 0 – 0.8 ML range in expanded scale.

Figure 6. Measured heat of Ag atom adsorption versus the average Ag particle size on Fe$_3$O$_4$(111) at 300 K. The Ag particle size is expressed as both the effective diameter and the number of Ag atoms already in the particle, both estimated assuming the Ag is in the form of 3D particles with a fixed density of $4 \times 10^{12}$ particles per cm$^2$, as measured by AES and LEIS. The diameter is estimated assuming hemispherical shape, an assumption also used in analyzing the AES and LEIS data.
Table of Contents Graphic: