

LETTERS

Interaction of Ag with MgO(100)

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The electronic and chemical properties of Ag clusters on MgO(100) films grown on Mo(100) were studied using metastable impact electron and ultraviolet photoelectron spectroscopies (MIES/UPS) and temperature programmed desorption (TPD). The work function of the as-grown and vacuum-annealed MgO(100) surfaces increases monotonically with increasing Ag coverage. In contrast, an initial decrease of the work function upon Ag deposition was found for the sputter-damaged MgO(100) surface, implying that small Ag clusters on this surface are electron deficient. Point defects with high electron affinities, such as F^{2+} and/or V/V^- centers, created by sputtering are believed to be responsible for the initial decrease of the work function upon Ag deposition. For low Ag coverages, the quantity of CO adsorbed at 80 K on a sputter-damaged MgO(100) surface is much greater than that adsorbed for a comparable Ag coverage on a relatively smooth, MgO(100) surface. These results are consistent with point defects on MgO(100) being responsible for altering the electronic and chemical properties of supported Ag clusters.

Defect sites are important for adhesion and nucleation of metal clusters on oxide catalyst supports, and can modify the electronic and chemical properties of adsorbed metal clusters.¹ Thus the nature of the interaction between metal clusters and defect sites of the support material is particularly important in developing a molecular-level understanding of supported metal catalysts.

Nanoclusters of Au, known to be inert in the bulk form, have attracted attention due to their extraordinary reactivities and selectivities for a variety of catalytic processes.² Recently, catalysts of highly dispersed Ag clusters have been shown to exhibit selective oxidation activities comparable to those of nanosized Au catalysts.³ Due to their special and technologically important properties, noble metal nanoclusters on oxide surfaces are receiving considerable attention.

The interaction of Ag with MgO surfaces has been studied extensively experimentally and theoretically. There is ample

evidence that Ag grows three-dimensionally on MgO(100)⁶⁻⁸ although layer-by-layer growth has been reported.^{4,5} Ag interacts weakly with a low-defect MgO(100) surface;⁹⁻¹¹ however, neutral or charged oxygen (F , F^+ , and F^{2+}) and magnesium vacancies (V , V^- , and V^{2-}) can enhance the interaction between MgO(100) and Ag.^{12,13}

In this paper we report modifications of the electronic properties of Ag clusters supported on MgO(100) by defect sites created by argon ion sputtering. The strong interaction between Ag and the defect sites leads to changes in the chemical properties of the Ag clusters, demonstrating that defect sites alter the properties of metal/oxide catalysts.

The experiments were carried out in an ultrahigh vacuum (UHV) system (base pressure of 1×10^{-10} Torr) consisting of two interconnected chambers. One chamber is equipped with low energy electron diffraction (LEED), temperature programmed desorption (TPD), and an ion sputtering gun. In the second chamber are facilities for Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and metastable

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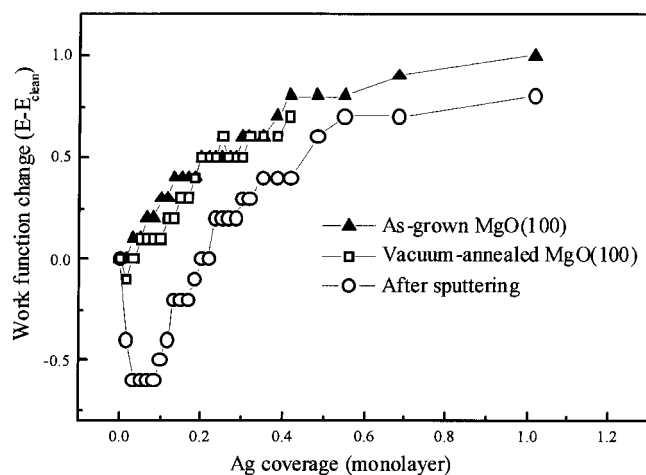


Figure 1. Changes of the work function for various MgO thin films as a function of Ag exposure.

impact electron and ultraviolet photoelectron spectroscopies (MIES/UPS). MIES is a nondestructive and extremely surface sensitive technique that uses metastable helium atoms as a surface probe.¹⁴ MIES/UPS data were acquired simultaneously using a cold-cathode discharge source^{15,16} that provides ultraviolet photons and metastable He 2^3S ($E^* = 19.8$ eV) atoms with thermal kinetic energy. Signals from metastable and photon excitation were separated by a time-of-flight method using a mechanical chopper. MIES and UPS data were acquired with the photon/metastable beams incident at 45° with respect to the surface normal. All MIES/UPS data are referenced to the Fermi level of the Mo(100) substrate.

The Mo(100) sample was cleaned by repeated cycling to 2200 K, and the sample cleanliness confirmed by AES. In addition, LEED of the clean surface exhibited a (1×1) periodicity with sharp spots and low background intensity. The MgO(100) films were prepared by depositing Mg in an O_2 background of 1×10^{-7} Torr with the Mo(100) substrate at 600 K (as-grown MgO). LEED of the as-grown MgO(100) film showed a (1×1) periodicity with diffuse spots and a high background intensity, indicating significant surface roughness. Multiple anneals at 1150 K resulted in a (1×1) -LEED pattern with sharp spots and a low background intensity (vacuum-annealed MgO).¹⁷ The Ag evaporation source consisted of a tungsten filament wrapped with an ultrahigh purity (99.99%) Ag wire. Before Ag deposition, the evaporation source was thoroughly outgassed and calibrated using AES.

The as-grown and vacuum-annealed MgO(100) surfaces as a function of increasing Ag coverage were studied using MIES/UPS. For the clean MgO surface, the O(2p) feature appears at 5.5 eV below the Fermi level. No F/F^+ defect features at 1–2.5 eV¹⁸ were observed with MIES, indicating that the number of F/F^+ centers is relatively small. Upon Ag deposition, the O(2p) feature in the MIES/UPS data attenuates, and the low-energy onset of the secondary electrons shifts, indicating a change in the work function. The Ag-induced features, observed in previous MIES/UPS studies by Kempter et al.,¹⁹ appear with increasing Ag coverages; however, relative to the O(2p) feature, the intensities of the Ag features were significantly smaller in the present study compared to that seen in the study of Kempter and co-workers.¹⁹

The variation of the work function versus Ag coverage for various MgO(100) surfaces is summarized in Figure 1. On the as-grown MgO film, the work function gradually increases with increasing Ag exposure. For the vacuum-annealed MgO(100) surface, the variation of the work function versus Ag coverage

differs little from that of the as-grown MgO film. The change in the work function versus Ag coverage on MgO(100) surfaces, then, is independent of the density of extended defect sites since in previous LEED and MIES studies, repeated annealing of this surface significantly reduces the number of extended defect sites.¹⁷

The study by Kempter et al., also reports that the work function of a MgO surface initially decreases at low Ag coverages, then increases as the Ag coverage is increased.¹⁹ Kempter et al. proposed that extended defects or Mg vacancies (V centers) are responsible for the formation of electron deficient Ag clusters at low Ag coverages.¹⁹ In the present study, however, this behavior was not observed for MgO(100) surfaces with small or large numbers of extended defects, indicating that extended defects are not responsible for the initial decrease of the work function at low Ag coverages.¹⁹

In contrast to the results from the as-grown and vacuum-annealed MgO(100) surfaces, the work function initially decreased upon Ag deposition after sputtering and heating the vacuum-annealed MgO(100) surface to 600 K (Figure 1). In this case, point defects, such as neutral and charged F and V centers created by sputtering, are likely responsible for the initial decrease of the work function with the addition of Ag.

No F/F^+ center features within the band-gap region were detected with MIES after sputtering, indicating that the number of the F/F^+ centers did not increase significantly upon sputtering.¹⁷ Thus it is unlikely that F/F^+ centers are responsible for the decrease of the work function at low Ag coverages. Furthermore, it is unlikely that F/F^+ centers, because of their rather low electron affinities,¹² will polarize Ag to $Ag^{\delta+}$. Oxygen vacancies created by sputtering can form F^{2+} centers, features not observed with MIES. The electron affinity of the F^{2+} centers, on the other hand, is sufficiently high to withdraw electron density from Ag to form $Ag^{\delta+}$.¹² Also it cannot be excluded that Mg vacancies (such as V/V^- centers) could lead to $Ag^{\delta+}$; however, previous studies have shown that sputtering preferentially removes oxygen from oxide surfaces, leading to an increase in the relative number of O vacancies compared to Mg vacancies on the sputter-damaged MgO surfaces.²⁰ It is noteworthy that previous electron paramagnetic resonance (EPR) studies have shown that small coverages of metals (M) such as Li, Mg, Na, Rb, and Cs on MgO can react with F^{2+} centers to form M^+ and F/F^+ centers.^{21–24}

Our results suggest that Ag atoms selectively interact with point defects on the surface at low Ag coverages, results consistent with theoretical studies showing a strong interaction between adsorbed metal atoms and point defects on MgO.^{12,13} Also, AFM studies have shown that the adhesion and nucleation of Pd on MgO(100) are controlled by point defects.²⁵

To investigate the chemical properties of Ag clusters on various MgO surfaces, TPD experiments were carried out using CO as a probe. The first MgO film used for the CO TPD experiments was grown at 600 K, followed by a brief anneal to 1100 K. Significant CO adsorption was observed at 80 K, indicating that the surface was highly defective (Figure 2). (CO does not adsorb on a defect-free MgO(100) surface at this temperature.^{26–28}) Two separate features are resolved in the CO TPD spectrum (Figure 2a), most probably from two different types of defect sites, e.g., steps and corners. Theoretical studies predict that the CO binding energy to a corner site is significantly higher than to a step.²⁹ Two defect-related features in the CO TPD spectrum from a MgO(100) thin film were reported by Kay et al.,²⁶ in agreement with the present work. As the Ag coverage is increased, the high-temperature feature

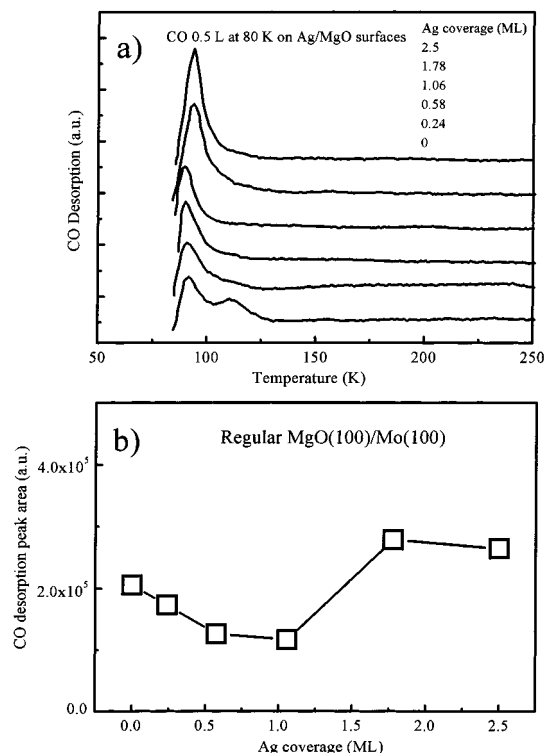


Figure 2. (a) CO TPD from various Ag/MgO surfaces after exposing 0.5 langmuir (langmuir: 1×10^{-6} Torr \times s) of CO at 80 K. CO exposures of 0.5 langmuir result in saturation at 80 K for all cases. The MgO thin film was prepared by deposition of Mg in an O_2 ambient environment of 1×10^{-7} Torr at a sample temperature of 600 K, followed by a brief flash to 1100 K. Ag was deposited at room temperature. (b) Summary of CO uptakes of Figure 2a.

attenuates, whereas the intensity of the 90 K feature remains constant. At higher Ag coverages, the high-temperature shoulder completely disappears, and the feature at 90 K grows.

CO TPD for the various Ag/MgO surfaces are shown in Figure 2a and their relative areas summarized in Figure 2b. At Ag coverages below 0.6 monolayer (ML), the amount of CO adsorbed decreases with increasing Ag coverages. The initial decrease in the CO coverage can be attributed to Ag clusters blocking defect sites on the MgO(100) surface to which CO adsorbs. At Ag coverages >1.0 ML, the amount of adsorbed CO increases (Figure 2b). Since CO does not adsorb on bulk Ag at 70 K,^{30,31} it is unlikely to adsorb on relatively large Ag clusters at 80 K. However, Ag atoms at the Ag–MgO interface may be chemically modified compared to bulk Ag due to rehybridization of the Ag-valence band with the O(2p) band of MgO.³² This electronic modification of the Ag could give rise to the increased stability of CO.

The MgO surface used for the CO TPD experiments shown in Figure 3a was prepared by sputtering a vacuum-annealed MgO(100) film, then flashing briefly to 600 K. In the data of Figure 3a, broad CO desorption features are apparent between 80 and 130 K. After deposition of a small amounts of Ag, the amount of CO adsorbed increases (see Figure 3b) by a factor of 2 compared to the clean MgO(100) surface of Figure 3a. With a further increase in the Ag coverage, the amount of CO adsorbed decreases. The chemical properties of Ag clusters formed at low Ag coverages on low-defect MgO(100), then, are significantly altered compared to similar Ag coverages on a ion-sputtered MgO(100) surface.

The work function measurements of Figure 1 indicate that Ag clusters on the sputter-damaged MgO(100) surface are to a degree positively charged at low Ag coverages. The larger

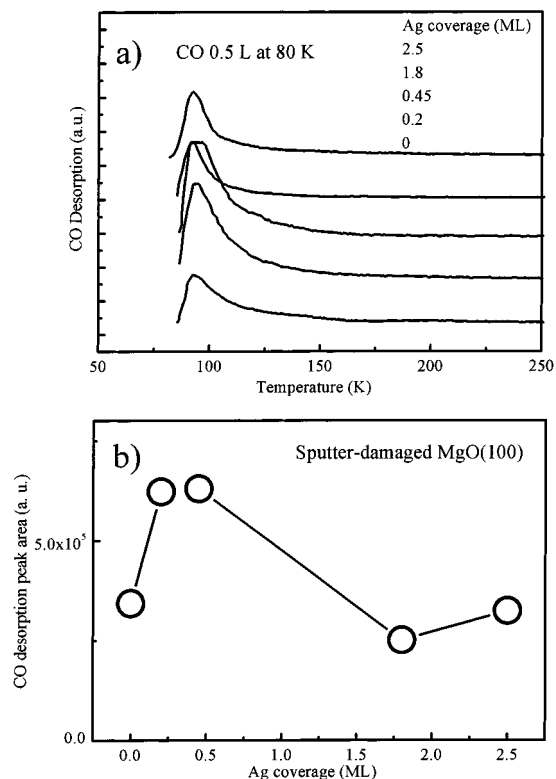


Figure 3. (a) CO TPD from various Ag/MgO surfaces after exposing 0.5 langmuir of CO at 80 K. Before Ag deposition, defect sites on the vacuum annealed MgO(100) thin films were created by sputtering at room temperature, followed by a brief flash to 600 K. Ag was deposited at room temperature. (b) Summary of CO uptakes of Figure 3a.

amounts of CO that adsorb on low Ag coverages on the sputter-damaged MgO(100) can be related to the electron deficient nature of Ag clusters on the sputter-damaged MgO(100) surface. Consistent with these results, it has been reported that CO interacts more strongly with Ag cations on a zeolite support than with neutral Ag atoms.³³

In conclusion, the work function changes of various MgO(100) films as a function of Ag coverage imply that the electronic properties of small Ag clusters can be significantly altered in the presence of point defects. The chemical properties of Ag clusters interacting with point defects, in turn, are quite different from those on defect-free MgO surfaces. Therefore, point defects must play a significant role in defining the catalytic properties of oxide-supported metal clusters.

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