Interaction of Silver, Cesium, and Zinc with Alumina Surfaces: Thermal Desorption and Photoemission Studies

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Cs, Ag, and Zn behave in a different way when deposited on surfaces of ultrathin (15–20 Å) films of alumina. In the case of CsAl₂O₃, the alkali atoms wet the oxide, forming strong chemisorption bonds. At small coverages of Cs, desorption of the alkali occurred between 600 and 1000 K. As the amount of Cs deposited increased, there was a reduction in the Cs desorption temperature to ~350 K. This broad range of desorption temperatures reflects a continuous decrease in the Cs adsorption energy from 63 to 18 kcal/mol with increasing Cs coverage. The deposition of small amounts of Cs induced large (0.9–1.1 eV) positive shifts in the binding energies of the O KVV, O 1s, and Al 2p features of the alumina films. This is consistent with a transfer of electrons from Cs into surface states of alumina that produces a transformation similar to a change from p-type to n-type semiconductors. Ag and Zn do not wet the surface of alumina well and form three-dimensional clusters or particles. In these systems, the activation energies for desorption of the admetal increase with cluster size (20 kcal/mol for Ag, 10 kcal/mol for Zn). The deposition of Ag and Zn induces only minor perturbations in the electronic properties of alumina. Small silver clusters supported on alumina exhibit an incompletely developed metallic band structure. The differences in the behavior of the CsAl₂O₃ and Ag/Al₂O₃ or Zn/Al₂O₃ systems are explained in terms of variations in the surface free energy of the admetals and in the nature of the admetal–oxide bonds.

I. Introduction

Most commercial catalysts consist of small metal particles supported on high-surface-area oxides. In these systems, the oxide may behave as an inert support or may actually modify the activity of the metal catalyst. Metal particles or adlayers on oxide surfaces are also relevant to crystal growth, gas sensor operation, bonding in composites, and the fabrication of devices in the microelectronics industry. Despite these technologically important applications, our understanding of the behavior of metal/oxide interfaces is rather rudimentary. This fact has motivated many studies investigating the interaction of metals with oxide surfaces in recent years.

The growth of metals on alumina surfaces has received considerable attention. Studies for the deposition of Pt, Rh, Cu, and Ag on α-Al₂O₃(0001) and Ag on α-Al₂O₃(1120) show poor wetting of the alumina surfaces by the admetals at 300 K. In all these systems, the admetal grows, forming three-dimensional (3D) islands or clusters (Volmer–Webber growth mode). For the deposition of Pd on α-Al₂O₃(0001) at 300 K, a layer-by-layer rise (Frank–Van der Merwe growth mode) of the metal film has been observed. The Pd film coalesces into 3D particles upon heating to temperatures above 600 K. Rh, Pd, and Pt particles toward small molecules (H₂, CO, NO, etc.) depends strongly on the size of the particles.

II. Experimental Methods

II.1. Instrumentation. The experiments were carried out in a conventional ultrahigh vacuum system (base pressure ≈ 3 × 10⁻¹⁰ Torr) equipped with instrumentation for TDS, photoemission, and ion-scattering spectroscopy (ISS). The photoemission spectra reported in section III were acquired using monochromatized Mg Kα radiation and a hemispherical electron energy analyzer with multichannel detection. In order to enhance surface sensitivity, the sample was positioned such that...
the takeoff angle for electron detection was 30° off normal. The binding-energy scale for the photoemission spectra was calibrated by setting the Zn 2p1/2, Cs 3d5/2, and Ag 3d5/2 core levels of the pure metals to binding energies of 1044.9, 726.6, and 368.0 eV, respectively. The experiments of ISS were performed using He⁺ as the incident ion and using a scattering angle of 90°. TDS measurements were carried out using a quadrupole mass spectrometer, which was housed in a differentially pumped liquid-nitrogen-cooled jacket that had a small aperture in the front. In this arrangement, the mass spectrometer detected only species that desorbed from the "front" face of the sample during the thermal desorption experiments.

The Mo(110) substrate was mounted on a manipulator capable of liquid-nitrogen cooling to 80 K and resistive heating to 1550 K. An electron-beam assembly provided the capability for heating to 2500 K. Temperatures were monitored with a (W–5% Re)/(W–26% Re) thermocouple spot-welded to the upper edge of the Mo(110) crystal. The crystal was cleaned according to standard procedures. The cleanliness of the surface was verified by means of X-ray photoelectron spectroscopy (XPS).

II.2. Preparation of Alumina Films. We followed two different routes to prepare the alumina films, and both produced films of the same quality as judged by the results of XPS, ISS, and the adsorption/desorption of Ag, Cs, and Zn. In the first procedure, aluminium atoms (generated by heating a W filament wrapped with a high-purity wire of Al) were dosed to the Mo(110) substrate in a background O₂ pressure of 10⁻⁵–10⁻⁶ Torr, with subsequent annealing to 1200 K to improve the crystalline quality of the film. This methodology has been used by several authors to grow ultrathin Al₂O₃ films on Mo(110) and other metal substrates.

In the second procedure, the Mo(110) substrate was initially exposed to NO₂ (5–50 L) at 950–1000 K and ultrathin films of molybdenum oxide were formed through the reaction: NO₂, gas + Mo → N₂, gas + MoOₓ. Then Al was vapor deposited on the molybdenum oxide film at 700 K and alumina was produced (Al + MoOₓ → Al₂O₃ + Mo). This was followed by annealing to 1200 K in ambient oxygen (10⁻⁷ Torr) for 2–5 min. The results of He-ISS spectra indicated that no Mo was present in the surface of these films, and the attenuation of the Mo 3d signal in XPS spectra pointed toward an epitaxial growth of alumina on the molybdenum substrate. The alumina films exhibited an O 1s peak in the range 532.1–532.4 eV and a binding-energy shift of 2.6–2.9 eV in the Al 2p features (for a typical result, see Figure 1). These are strong indications of the formation of stoichiometric Al₂O₃.

The experiments described in section II.3 were carried out over alumina films that were 15–20 Å thick (as determined from the intensity of the Mo 3d and Al 2p signals in the corresponding XPS spectra).

II.3. Admetal Deposition. Silver and zinc were deposited by sublimation from high-purity wires of Ag and Zn, which were heated by W filaments. The atomic flux from the metal dosers was calibrated according to the methodology described in our previous studies for Ag/Mo(110) and Zn/Mo(110). In this work, the amount of Ag or Zn dosed is reported with respect to the number of Mo(110) surface atoms. One equivalent monolayer (ML) of the admetal corresponds to the deposition of 1.43 × 10¹⁵ atoms cm⁻² of Ag or Zn. Cesium was vapor-deposited from a SAES getter chromat source. The metal dosers were outgassed thoroughly prior to vapor deposition.

III. Results

III.1. Interaction of Silver and Alumina. On clean Mo(110) at 300 K, silver grows layer-by-layer. The corresponding TDS spectra display Ag desorption temperatures that increase from 1020 to 1075 K when the Ag coverage is raised from 0.2 to 1.0 ML. For Ag multilayers deposited on clean Mo(110), the onset of desorption appears at ∼850 K. Figure 2 shows Ag thermal desorption spectra acquired after depositing silver at 300 K on an alumina film (bottom panel) and on a Mo(110) surface covered with a saturated layer of chemisorbed oxygen (top panel). The TDS results for Ag/O/Mo(110) surfaces indicate that the oxygen overlayer prevents the formation of Mo–Ag bonds. The Ag desorption features from O/Mo(110) match well those seen for Ag multilayers on clean Mo(110) or other metal substrates, with a common leading edge and a line shape typical of zero-order desorption kinetics. This behavior is consistent with the formation of large 3D clusters or islands of silver on the O/Mo(110) surface.

In Figure 2, the desorption of silver from the alumina film occurs between 800 and 1000 K. The Ag desorption features do not show the common leading edge expected for zero-order desorption kinetics. This is very clear at low coverages of the admetal, where there is a shift toward higher temperature in the complete Ag desorption peak as the Ag coverage increases. An identical phenomenon was observed in spectra for the desorption of silver from alumina films supported on Ru(001) and on α-Al₂O₃(1120) single crystals. A complete analysis of these Ag desorption data yielded activation energies for desorption (30–60 kcal/mol) that were smaller than the heat of...
sublimation of silver (68 kcal/mol) and yielded a fractional order (0.6 - 0.8) for the dependence of the desorption rate on Ag coverage. The trends seen in Figure 2 for the desorption of Ag from alumina are in good agreement with trends found in Monte Carlo simulations for the desorption of islands (or particles) from a surface. Small particles will desorb more easily than “infinite” particles owing to differences in surface tension. An atom at the edge of a small island has fewer nearest neighbors than in the bulk of an “infinite” island, so it desorbs more easily than the atoms in an “infinite” island. As a result, the TDS peaks shift to lower temperatures with decreasing coverage when small islands are formed.

The TDS data in Figure 2 indicate that the 3D clusters formed after depositing Ag on the O/Mo(110) surface are of bigger size than those formed on the alumina film. One can reach an identical conclusion after examining the results of XPS experiments.

Figure 3 shows Ag 3d XPS spectra recorded after depositing 1.3 ML of Ag on the alumina film used to obtain the TDS data in Figure 2. Annealing from 330 to 700 K (close to the onset of silver desorption) leads only to minor changes (<10%) in the intensity and position of the Ag 3d peaks. This indicates that the small Ag clusters formed at 330 K are neither diffusing into the bulk of the alumina substrate nor forming large 3D particles upon heating (i.e., sintering). For the deposition of 1.6 ML of Ag on the O/Mo(110) surface, one finds a Ag 3d intensity smaller than that seen after depositing 1.3 ML of Ag on the alumina film, and the silver signal in the Ag/O/Mo(110) system decreases considerably (~40%) after heating from 330 to 700 K (see bottom of Figure 3). These results are consistent with the formation of large 3D clusters of silver on the O/Mo(110) surface. Therefore, it is not surprising that the Ag/O/Mo(110) and Ag/alumina systems show a different behavior in TDS experiments.

Figures 4 and 5 display core- and valence-level photoemission spectra acquired after depositing several coverages of silver on an alumina film at ~300 K. A surface with 0.3 ML of silver exhibits Ag 3d peak positions that are shifted ~0.6 toward higher binding energy with respect to those of bulk metallic Ag (374.0 and 368.0 eV). As the silver coverage increases, there is a monotonic decrease in the Ag 3d binding energies until the values for pure Ag are reached at θAg = 9.1 ML. Similar negative binding-energy shifts were observed in the centroid of the Ag 4d band and in the Ag MVV Auger transition (not shown). The binding-energy shifts in Figure 4 cannot be attributed to the formation of Ag–O bonds, since the Ag 3d core levels of Ag2O and AgO appear 0.4–0.7 eV at lower binding energies than those of metallic Ag. Ag atoms deposited on Al(100) show binding-energy shifts similar to those in Figure 4, but the Ag desorption temperatures in Figure 2 are not consistent with the possible presence of Ag–Al bonds. Thus, the binding-energy shifts in Figure 4 probably come from changes in final-state relaxation energy. In a “bulk” metal the screening of the photoemission core-hole is more effective than in an oxide or small metal particles. Therefore, when the Ag coverage increases in the Ag/alumina systems, there is
an “apparent” shift toward lower binding energy in the Ag 3d levels and 4d band.

In the bottom of Figure 4, we can see valence band spectra for a series of Ag/alumina surfaces. Since the valence region was examined using Mg Kα radiation, the intensity of electron emissions from the alumina bands is very weak, and the valence spectra are dominated by electron emissions from the Ag bands. For a surface with 0.3 ML of Ag, emissions from the Ag 4d band appear from 4.5 to 7.5 eV, with a band centroid located around 6 eV. This is very different from the band structure of metallic Ag, 34 where the 4d band extends from 3 to 8 eV and is dominated by a strong peak at ∼4.5 eV. As the Ag coverage increases in Figure 4, the band structure of the supported Ag clusters evolves toward that of bulk Ag. There is a clear rise in the density of states in the 4.0–4.5 eV region, and the full-width at half-maximum of the 4d band increases from 2.4 eV at 0.3 ML to 2.9 eV at 1.0 ML and finally to 3.3 eV at 9.1 ML.

Figure 5 illustrates how the Al 2p and O 1s core levels of an alumina film change after the adsorption of silver. The deposition of 0.3 ML of Ag induced negligible changes in the Al 2p and O 1s peaks of the film. For a film with 2.4 ML of Ag, there is a reduction of ∼15% in the intensity of the Al 2p and O 1s features (without significant changes in peak positions). This small reduction is consistent with the formation of 3D clusters of Ag on top of the alumina film. After depositing 9.1 ML of Ag, one sees a large attenuation in the Al 2p and O 1s signals with very small (0.10–0.15 eV) negative binding-energy shifts, which can be attributed to an increase in the final-state relaxation energy within the escape depth probed by XPS. 33

III.2. Interaction of Cesium and Alumina. In general, cesium shows a much larger affinity toward oxygen than silver. 35 Forming oxides with a much bigger thermal stability (Ag2O, ΔHf = −7.3 kcal/mol; Cs2O, ΔHf = −75.9 kcal/mol 19). This leads to very important differences in the nature of the Ag ↔ Al2O3 and Cs ↔ Al2O3 interactions.

Figure 6 shows thermal desorption spectra taken after adsorbing different amounts of cesium on an ultrathin (∼20 Å) alumina film at 80 K. XPS spectra indicated that no cesium was left on the alumina after heating to 1100 K. At small doses of Cs desorption occurred between 600 and 1000 K. As the amount of cesium deposited increased, there was a large reduction in the cesium desorption temperature. The Cs desorption peak at ∼320 K grew continuously without saturation and agrees well with the desorption temperature observed in previous studies of cesium multilayers. 36 On the other hand, the Cs desorption features between 400 and 1000 K can be assigned to the desorption of Cs atoms that were strongly bound to the alumina. The broad range of desorption temperatures seen in Figure 6 reflects a continuous decrease in the Cs adsorption energy from 63 to 18 kcal/mol. 37 A similar phenomenon has been reported for the adsorption of Cs on metal surfaces 36 and on TiO2(110) 4a,38 and has been attributed to a reduction in the ionicity of the Cs–substrate bond with increasing Cs coverage due to dipole–dipole repulsion. 4,39 TDS spectra acquired during the decomposition of CsOx films show desorption of cesium at temperatures from 700 to 1000 K. 40 Thus, in Figure 6, the Cs desorption features between 700 and 1000 K could come from the decomposition of oxide compounds in which Cs is sharing O atoms with Al.

Figure 7 displays photoemission spectra recorded after depositing cesium on an alumina film at 80 K. In the top panel of the figure, we can see the O KVV Auger transition for alumina (755–735 eV region) and the 3d peaks for cesium (755–723 eV region). In the Cs 3d spectrum of the cesium...
multilayer, the two sharp peaks at 726.6 and 740.5 eV are the main 3d levels whereas the broad shoulders toward higher binding energy correspond to plasmon losses. A direct comparison of the Cs 3d peak positions for the Cs multilayer and Cs atoms bonded to alumina is ambiguous owing to changes in the final-state relaxation energy. However, it is clear that the Cs 3d\textsubscript{5/2} spectra in Figure 7 for the submonolayer Cs/alumina systems do not show a plasmon structure. Thus, we can conclude that the Cs atoms bonded to alumina are not in a metallic state. The deposition of small amounts of Cs induced large (0.9–1.1 eV) positive shifts in the binding energies of the O KVV (Figure 7), O 1s (Figure 7), and Al 2p (not shown) features of the alumina film. In Figure 7, as the Cs coverage increases in the Cs/alumina systems, there is a simultaneous and almost identical shift in the O KVV, Cs 3d, and O 1s levels toward higher binding energy. This may be a consequence of changes in the Fermi level of the film within the bandgap due to the transfer of electrons from Cs into surface states of alumina. Similar binding-energy shifts are observed when doping semiconductors and switching from p-type to n-type materials. To induce this transformation, only small concentrations of the doping agent are necessary.

Figure 8 shows photoemission spectra acquired after annealing an alumina film covered with a cesium multilayer from 80 to 1200 K. Heating to 350 K induces the desorption of the Cs multilayer, and only Cs atoms that are bonded to alumina are left on the sample (see Figure 6). At this point the Cs 3d\textsubscript{5/2} peak is broad, indicating that more than one type of Cs species is present on the surface. Further heating to 1000 K leads to desorption of most of the Cs, with subsequent large negative shifts in the binding energy of the O KVV, O 1s (not shown), Al 2p, and Cs 3d features. Upon annealing to 1200 K, all the cesium has desorbed, and the Al 2p, O 1s and O KVV spectra are now very similar to those obtained for the alumina film before the deposition of cesium.

The results in this section indicate the Cs \textrightarrow Al\textsubscript{2}O\textsubscript{3} interactions are much stronger than the Ag \textrightarrow Al\textsubscript{2}O\textsubscript{3} interactions, as can be expected from the difference in the thermal stability of cesium–oxygen and silver–oxygen compounds. Cesium wets alumina...
surfaces and induces large changes in the electronic properties of the oxide.

### III.3. Interaction of Zinc and Alumina

Zinc forms oxides that exhibit a thermal stability comparable to that of cesium oxides. However, the Zn \( \leftrightarrow \) Al\( _2 \)O\( _3 \) interactions are much weaker than the Cs \( \leftrightarrow \) Al\( _2 \)O\( _3 \) and Ag \( \leftrightarrow \) Al\( _2 \)O\( _3 \) interactions. For example, the sticking coefficient of silver on alumina films and on a \( \alpha \)-Al\( _2 \)O\( _3 \)(1120) surface is close to 0.85 at 300 K. At this temperature, we were unable to adsorb zinc on alumina films supported on Mo(110). Significant sticking of zinc to the oxide surfaces was seen only when the temperature of the sample was below 250 K. Cadmium, like zinc, has a low sticking probability on oxides at room temperature.

Figure 9 shows zinc thermal desorption spectra acquired after depositing an ultrathin (\( \sim \)20 Å) alumina film at 80 K. The coverages of Zn are 0.3, 0.8, 1.7, and 4.2 ML. Heating rate = 5 K/s.

The results of photoemission experiments also indicate that the Zn \( \leftrightarrow \) Al\( _2 \)O\( _3 \) interactions are relatively weak. Figure 10 displays Zn LMM Auger and Zn 2p\( _{1/2} \) XPS spectra for a series of Zn/alumina surfaces. The deposition of Zn and acquisition of the spectra were performed at 80 K. In the Zn 2p\( _{1/2} \) spectra,
there is a binding-energy shift of about −0.5 eV when the Zn coverage is increased from 0.3 to 4.2 ML. The spectrum for θ_Zn = 4.2 ML exhibits a peak position (1045.0 eV) that is close to that of bulk metallic Zn (1044.9 eV\textsuperscript{22}). The binding-energy shifts in the Zn 2p\textsubscript{1/2} spectra could be attributed to the formation of ZnO\textsubscript{3} at low coverages of the admetal.\textsuperscript{46} However, this hypothesis can be ruled out on the basis of the peak positions seen in the Zn LMM spectra of Figure 10. In zinc oxides the Zn L\textsubscript{3}M\textsubscript{4.5}M\textsubscript{4.5} features appear at a kinetic energy of \textasciitilde 988 eV\textsuperscript{47,48} whereas for the Zn/alumina surfaces these features appear between 992 and 993 eV. Thus, the binding-energy shifts in Figure 10 probably come from changes in the final-state relaxation energy that accompany the growth of metal clusters and/or an oxide(insulator)-to-metal(conductor) transition within the escape depth probed by XPS.\textsuperscript{33} The adsorption of zinc induced only very minor (<0.1 eV) negative shifts in the position of the Al 2p and O 1s peaks of the alumina substrate. The behavior seen for the Zn/alumina surfaces is similar in many aspects to that found for the Ag/alumina surfaces, where the admetal wets the alumina substrate poorly and has, therefore, only a minor influence on the electronic properties of the oxide.

IV. Discussion

The data presented above for the cesium/alumina systems indicate that the alkali atoms wet the oxide, forming strong chemisorption bonds. Studies examining the adsorption of alkalis on TiO\textsubscript{2}, Cr\textsubscript{2}O\textsubscript{3}, and ZnO show that the alkali atoms spread out on the surface of these oxides, occupying in many cases specific sites provided by the oxide lattice.\textsuperscript{4,9,49,50} For the interaction of alkalis with single-crystal faces of oxides, well-ordered overlayers have been observed.\textsuperscript{5} For example, STM images for Na deposited on TiO\textsubscript{2}(110) show a dispersed adlayer that forms p (4 \times 2) and c (4 \times 2) structures with increasing alkali coverage.\textsuperscript{9,50} These structures are a consequence of repulsive forces between the alkali adatoms.\textsuperscript{4,9a} Up to relatively high coverages of the admetal, one can expect a shift (or polarization) of electron density from the alkali atoms toward the oxide substrate.\textsuperscript{4,9a} To minimize dipole \textsuperscript{\leftrightarrow} dipole repulsion, the alkali adatoms move apart on the surface, forming well-defined structures. The alkali \textsuperscript{\leftrightarrow} alkali repulsion also affects the adsorption energy of the alkali.\textsuperscript{4} Our results for Cs/Al\textsubscript{2}O\textsubscript{3} and data for Cs/TiO\textsubscript{2}(110)\textsuperscript{4a,38} show a reduction of 30–45 kcal/mol in the adsorption energy of cesium when one goes from systems with low coverage to a saturated adlayer of cesium.

Silver and zinc do not wet the surface of alumina well and form 3D clusters or particles. This behavior is similar to that reported for Cu, Pt, Pd, and Rh films supported on α-Al\textsubscript{2}O\textsubscript{3}(0001).\textsuperscript{5,17} In the case of silver, such a behavior is not surprising, since the metal, in general, has a low affinity toward oxygen.\textsuperscript{5,15a} On the other hand, the behavior of zinc is difficult to explain because this metal forms stable oxides\textsuperscript{19} with a stability comparable to that of cesium oxides.\textsuperscript{42} Previous studies investigating the interaction of a series of metals with TiO\textsubscript{2}(110) show that the wetting ability of the admetal increases when its affinity toward oxygen rises.\textsuperscript{15} Thus, admetals that form oxides with heats of formation similar to those of zinc oxides (Na, Cs, Fe, Mn) wet the TiO\textsubscript{2}(110) surface, whereas poor wetting is observed for the deposition of metals that form oxides with relatively small heats of formation (Cu, Pd, Pt, Au).\textsuperscript{4,15}

To explain the differences in the behavior of the Cs/alumina and Zn/alumina systems, one must consider differences in the surface free energy of the admetals and in the nature of the admetal–oxide bonds. In principle, the adhesion energy (E\textsubscript{adh}) of a metal on an oxide is given by\textsuperscript{4,11c}

\[ E_{\text{adh}} = \gamma_{\text{metal}} + \gamma_{\text{oxide}} - \gamma_{\text{metal/oxide}} \]

where \( \gamma_{\text{metal}} \) and \( \gamma_{\text{oxide}} \) are the surface energies of the metal and oxide, respectively, and \( \gamma_{\text{metal/oxide}} \) is the metal/oxide interfacial energy. If \( \gamma_{\text{metal/oxide}} \geq \gamma_{\text{metal}} - \gamma_{\text{oxide}} \), then the metal will wet the oxide surface.\textsuperscript{5} Since the surface energy of metals is usually larger than that of oxides,\textsuperscript{51} there must be very good bonding at the metal/oxide interface for wetting to occur.\textsuperscript{4} Cesium exhibits a extremely low surface energy (0.07 J m\textsuperscript{−2}), which is much smaller than those of alumina (0.9 J m\textsuperscript{−2}), zinc (0.94 J m\textsuperscript{−2}), and silver (1.30 J m\textsuperscript{−2}). Thus, on the basis of differences in surface free energy, the wetting ability of the admetals investigated in this work should follow the order Ag < Zn < Cs. In the cases of Ag and Zn, wetting will be highly dependent on the strength of the Ag–Al\textsubscript{2}O\textsubscript{3} and Zn–Al\textsubscript{2}O\textsubscript{3} bonds.

In Figure 11, we compare the relative positions of the valence s orbitals of Cs, Ag, and Zn with respect to the bands of alumina.

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Figure 11. Left: Energy positions for the bands of alumina\textsuperscript{53} and the valence s orbitals of atomic Cs, Ag, and Zn.\textsuperscript{54} The energies are reported with respect to the vacuum level. The hatched areas denote fully occupied states or bands. For atomic Zn the 4s shell is completely filled, whereas the Ag(5s) and Cs(6s) shells are only half occupied. The label “SS” refers to surface states in alumina.\textsuperscript{53} Right: Interaction between the O 2p band of alumina and the valence s band of Cs, Ag, and Zn adlayers.
interactions favored interface formation. We will analyze the repulsive closed-shell interactions were found to be a destabilizing factor, while alumina(Al 3s,p) attractive interactions and strong alumina(SS/Al 3s,p) bonds according to this line of thought.

The valence s orbitals of Cs are much less stable than those of Ag or Zn (see Figure 11). This favors “charge-transfer interactions” between the Cs(6s) orbitals and the empty surface states or bands of alumina, making the Cs—Al 2 O 3 bonds according to this order of 0.8 eV. As the Cs coverage increases, there is a reduction in the Cs desorption temperature from 1000 to 300 K. This reflects a continuous decrease in the Cs adsorption energy from 63 to 18 kcal/mol. The deposition of small amounts of Cs induces large (0.9—1.1 eV) shifts in the binding energies of the O KVV, O 1s, and Al 2p features of alumina. This is consistent with a transfer of electrons from Cs into surface states of alumina that produces a transformation similar to a change from p-type to n-type semiconductors.

(2) Silver does not wet the surface of alumina well and prefers to form 3D clusters on this oxide. Small silver clusters supported on alumina show Ag 3d and 4d binding energies larger (0.4—0.6 eV) than those of pure metallic silver. At the same time, the clusters exhibit a narrower valence d band. The activation energy for desorption of Zn increases with cluster size varying in the range from 20 to 30 kcal/mol.

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(45) These energies were calculated using the Redhead’s equation for first-order desorption kinetics37 with a pre-exponential factor of $10^{13}$ s$^{-1}$, a heating rate of 5 K/s, and desorption temperatures of 375 (θ$_{2c}$ = 0.3) and 435 K (θ$_{2c}$ = 4.2).
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