Interaction of Aluminum with the Ru(0001) Surface and Its Influence upon CO Chemisorption

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The interaction of vapor-deposited Al with the Ru(0001) surface and its influence upon CO chemisorption has been studied in ultrahigh vacuum by use of Auger electron spectroscopy, thermal desorption mass spectroscopy, and low-energy electron diffraction (LEED). Below 670 K, the Al grows as an overlayer in (111) oriented islands. By 1170 K, Al penetrates the surface to form intermetallic compounds with the Ru, and a ($\sqrt{3}$x$\sqrt{3}$)R30° LEED pattern dominates the surface structure. This is interpreted in terms of a stoichiometric monolayer of the compound Al$_2$Ru. Thermal desorption data indicate that this monolayer alloy has a heat of formation of about -24 kcal/mole, compared to -4 kcal/mole for the multilayer alloy which nucleates at higher coverages. The CO/Ru interaction at the surface of these intermetallic compounds is not very different from that on the clean Ru(0001) surface, except for the expected dilution of Ru sites by the added Al. In contrast, when the Al overlayer has not yet been annealed and the Al adatoms still sit on top of the Ru(0001) surface, they have a very strong influence upon CO desorption spectra. A new CO desorption state at 850-1050 K appears at submonolayer Al coverages, which is attributed to strong, direct interaction between adsorbed CO and Al probably involving C-O bond cleavage.

I. Introduction

Chemisorption and reactions on bimetallic or alloy surfaces are of fundamental interest in catalysis, corrosion prevention, and numerous other technological areas. In addition, understanding bimetallic surface chemistry is germane to the study of interactions between a metal catalyst (e.g., Ru) and its supporting metal oxide (e.g., Al$_2$O$_3$). Presently, a great deal is known of the interactions of simple molecules with single-element metal surfaces. In contrast, relatively little of a systematic nature is known of chemisorption on bimetallic surfaces. In this study, we investigate the interaction of CO with Al/Ru bimetallic surfaces generated by vapor-depositing Al on the Ru(0001) surface, in some cases followed by annealing to generate the intermetallic compound Al$_2$Ru at the surface. In the paper that follows, Chen, Crowell, Ng, Basu, and Yates explore the interactions of CO with Ni/Al bimetallic surfaces.

The interaction of CO with clean Ru(0001) has been well studied by a number of authors (refs 2-13 and references cited therein). It adsorbs molecularly and saturates at room temperature with a coverage $\theta_{CO}$ of 0.58 (per Ru surface atom). It desorbs intact in two distinct peaks (both $\beta_1$ and $\beta_2$) at 280 and 450 K, which reflect strong, short-range lateral CO-CO repulsions. On Al, CO also adsorbs molecularly, but with a much weaker bond than on Ru. It desorbs intact already at 1170 K. In this study, we find that Al on Ru(0001) induces a much stronger interaction with CO than with either clean metal surface. On the other hand, when Al is actually imbedded in the topmost Ru layer (i.e., in Al$_x$Ru alloy surfaces), its major effect on the CO/Ru interaction is simply to dilute the Ru sites on the surface. In the former case, we show evidence which suggests that Al directly participates in CO dissociation, perhaps by attacking the oxygen end of the molecule. A similar interaction is also suggested for CO on Ni/Al surfaces in the accompanying paper by Chen and co-workers, who interpret vibrational data in terms of a Ni$_x$C-O-Al$_y$ species which is a precursor to CO dissociation.

II. Experimental Section

The apparatus used for these experiments has been described in detail previously. Aluminum was vapor-deposited from a source described previously, where now a small Al wire was wound on a resistively heated tungsten wire. The cleaning procedures for the Ru(0001) surface where the same as we have used in our previous studies with this surface. Coverages here are normalized to the Ru(0001) surface atom density. (24$\theta_1$ corresponds to 1.64 x 10$^{14}$ cm$^{-2}$.) A gas doser was used for CO dosing, and exposures are reported here in units which have been approximately calibrated with CO uptake on clean Ru(0001).

III. Results

III.1. Interactions of Al with Ru(0001). Figure 1 shows thermal desorption mass spectra (TDS) of Al at $m/e$ 27 following increasing exposures of Al to Ru(0001) at room temperature. At low Al coverages, a desorption peak at ~1570 K appears, which broadens to lower temperature with increasing coverage. The peak maximum decreases to ~1530 K, and then a second desorption peak at ~1480 K appears, which also shifts to lower temperature with increasing coverage until it reaches a minimum temperature of ~1420 K. The peak then grows continuously in zero-order fashion, with a low-temperature edge that is independent of increasing Al coverage. This is characteristic of some type of multilayer Al or Al/Ru alloy that decomposes to liberate Al gas.

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The variation in the A1(68 eV)/Ru(273 eV) AES peak-to-peak ratio with A1 coverage at 300 K is shown in Figure 2. Also shown are the results after briefly (5 s) annealing the overlayers to 1170 K. Both the annealed and unannealed AES ratios are very similar below $\theta_{Al} \approx 0.7$, indicating a roughly linear increase in the ratio with A1 coverage. The AES signal growth shows a break in slope, and for the annealed surface it becomes almost constant when $\theta_{Al}$ exceeds 0.7. This is just the coverage when the multilayer peak begins to appear in the AI TDS. The signal decrease after an-

This leading edge was analyzed for the highest coverages ($\theta_{Al} > 3$) in zero-order Arrhenius form and gave a straight line fit with a desorption activation energy of 88 ± 4 kcal/mol. Since this is significantly larger than the heat of vaporization of pure Al at 1300 K ($\approx 71$ kcal/mol$^{17}$), we can conclude that Al desorption in the low-temperature ($\approx 1420$ K) peak is not from a multilayer of pure Al. (Note that pure Al melts at $\approx 933$ K$^{17}$.) Instead, it must represent the decomposition of some Al/Ru alloy or intermetallic compound. Mixtures of Al and Ru form a whole series of immiscible intermetallic compounds from AlRu to $\sim$ Al$_2$Ru$^{18,19}$ any of which could be responsible for the low-temperature (multilayer) desorption peak. The high-temperature TDS peak then reflects desorption from the first monolayer of Al at (in) the Ru surface. Its desorption temperature of 1570-1530 K then reflects an activation energy for desorption of $\approx 100$-97 kcal/mol, assuming a typical preexponential factor for desorption of $10^{13}$ s$^{-1}$ in first-order Redhead analysis.$^{20}$

Following desorption to 1640 K, no Al was observable on the Ru surface by Auger electron spectroscopy (AES), and the low-energy electron diffraction (LEED) pattern was identical with the p(1 x 1) pattern of the clean Ru(0001). Furthermore, subsequent CO TDS spectra were identical with that from freshly cleaned Ru(0001). These results indicate that Al removal by desorption was quantitative by 1640 K. Since our Al dose rate was somewhat unstable, we have used the integrated area under the AI TDS spectra as proportional to $\theta_{Al}$ here. Absolute coverage calibration will be described below.

The AES spectra for several AI coverages showing irreversible changes near 60 eV in the Al(LVV) line shape upon annealing briefly from 300 to 1170 K. Dashed line indicates region of change.

Even below $\theta_{Al} = 0.7$, the anneal to 1170 K resulted in a change in the Al(LVV) AES line shape in the region from 56 to 64 eV, as can be seen in Figure 3. This indicates a change in the valence energy levels of the Al atoms. That is, the chemical bonding of Al at the Ru interface changes distinctly upon annealing to 1170 K.

A survey of LEED observations for the annealed and unannealed Al/Ru(0001) overlayers is summarized in Figure 2. At 300 K, diffuse extra spots appear just inside the (01) spots of the Ru lattice at a coverage of $\approx 0.4$. These increase in sharpness and intensity with Al coverage. They can be easily explained on the basis of (islands of) an Al(111) film growing epitaxially and rotationally commensurate with the Ru(0001) surface. Annealing to 670 K only sharpens these extra spots and, in the range 0.67 $\leq \theta_{Al} \leq 1.9$, leads to the appearance of extra satellite spots due to the 13th-order coincidence lattice formed by the Al(111) overlayer ($a = 2.862$ Å) on the Ru(0001) surface ($a = 2.649$ Å). All Al(111) structure disappears upon annealing to 1170 K, and a (\sqrt{3} x \sqrt{3})R30° pattern is apparent for all AI coverages studied above 0.3. This pattern is sharpest and most intense when $\theta_{Al} \approx 0.7$ (i.e., when the monolayer peak saturates in AI TDS). When $\theta_{Al} > 1.2$, additional spots also appear in the LEED patterns of the annealed overlayers. These are complex and generally consist partially of doublets in the vicinity of the spot positions expected.

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(20) Redhead, P. A. Vacuum 1962, 12, 203.
for a (2 × 2) structure. We will refer to these collectively as "(2 × 2)" below.

The (√3 × √3)R30° pattern will be interpreted in terms of a hexagonal-close-packed plane of the intermetallic compound Al₂Ru, which is shown in Figure 4. This compound has the orthorhombic TiSi₂(C54) type structure, with a = 8.015, b = 4.715, and c = 8.780 Å. The lattice consists of (nearly) hexagonal layers such as shown in Figure 4, stacked one on another in an unusual packing arrangement. In the plane shown, the Al–Ru nearest-neighbor distances are 2.67 and 2.72 Å. This can be compared to the Ru–Ru distance of 2.649 Å in the Ru(0001) plane. Thus, this Al₂Ru plane needs only to be compressed by 4.715 Å in one direction and 2.649 Å in the other direction in order for this structure to match perfectly the observed hexagonal (√3 × √3)R30° LEED pattern. In this model, a single Al₂Ru layer then corresponds to a coverage θAl = 2/3.

The first appearance of the (√3 × √3)R30° LEED pattern for the annealed surface already at a coverage of θAl = 0.3 is consistent with islands of some Al/Ru intermetallic compound begin to nucleate and grow, but that large regions of the Al₂Ru structure over most of the surface, with penetration of thicker alloy layers such as shown in Figure 4. With increasing coverage, the low-temperature desorption peak appears, and eventually additional "2 × 2" structure shows up in LEED along with the √3 structure. These results indicate that thicker islands of some Al/Ru intermetallic compound begin to nucleate and grow, but that large regions of the Al₂Ru structure (Figure 4) still exist. The structure of the thicker compound is not yet known.

The AES uptake curves to Figure 2 are consistent with this model as well. At 300 K, a true Al film grows above the Ru, and the Al/Ru AES ratio grows continuously. For all coverages above ~0.7, however, annealing to 1170 K results in a nearly constant AES ratio. This would indicate a constant monolayer of the Al₂Ru structure over most of the surface, with penetration of thicker alloy islands at isolated nucleation sites which cover only a small part of the surface.

III.2. Influence of Al upon CO/Ru(0001) Interactions. In this section we will compare thermal desorption spectra for saturation exposures of CO to Al adlayers predeposited at 300 K, without (Figure 5) and with (Figure 6) prior anneal to 1170 K. In all these experiments, the CO exposure was ~12 langmuirs (1 langmuir = 10⁻⁶ Torr·s) at 150 K, which is beyond that required for saturation coverage (θCO ~ 0.58-0.67) on clean Ru(0001). Figure 5 shows typical TDS results for the unannealed Al/Ru(0001) interface. The well-known β₂/β₃ doublet characteristic of clean Ru(0001) is seen in the absence of Al.

With increasing Al coverage, the β₂/β₃ doublet narrows to a singlet and decays in intensity. Simultaneously, a new high-temperature peak (γ) grows and decays with increasing Al coverage. The γ peak shifts from 830 to 1050 K. Surface analysis by AES after desorption to 1170 K showed no oxygen or carbon, indicating that CO removal via desorption was quantitative by 1170 K. The integrated areas under the (β₂ + β₃) doublet and the γ peak are shown in Figure 7 as a function of Al coverage. The total (β₂ + β₃ + γ) CO desorption amount is shown in Figure 8 as a function of θAl. The (β₂ + β₃) area drops precipitously with θAl and the peak is essentially gone by θAl = 0.7. The γ peak does not grow until a coverage of 0.1, at which point it rises rapidly to a maximum at θAl = 0.7, and then drops to nearly zero by θAl = 1.4. The γ-area maximum corresponds to roughly 60% of the saturation CO coverage that will adsorb at 300 K on clean Ru.
at the surface for bonding to CO after annealing. This would indeed be consistent with the growth of alloys of structure such as that shown in Figure 4, where the topmost surface layer offers both Al and Ru atoms in large concentrations.

If, for the annealed surfaces, the CO TDS experiment for a given Al coverage was repeated by terminating the first TDS at 1170 K, cooling to room temperature and again adsorbing CO, the same CO TDS spectrum resulted. Furthermore, no species other than Al and Ru were observable by AES after desorbing the CO to 1170 K. These results also indicate that, for the annealed surface, the removal of CO via desorption is quantitative by 1170 K.

IV. Discussion

Let us first discuss the Al/Ru interface structures for the annealed and unannealed surfaces. The Al(111) LEED features and the AES uptake curves both indicate that, at room temperature, the Al grows on top of the Ru substrate. Thus, at low coverage, the Al goes down as adsatoms above the undisturbed Ru(0001) surface. The appearance of Al(111) features already at $\theta_{\text{Al}} \geq 0.4$ indicates a tendency for these adsatoms to coalesce into two- or even three-dimensional Al(111) islands. After a 670 K anneal, the clear observation of coincidence satellites in the range $0.7 < \theta_{\text{Al}} < 1.9$ shows that indeed a two-dimensional (one- or two-layer-thick) Al(111) film grows epitaxially on the Ru(0001) substrate. On further annealing to 1170 K, however, a marked transition to alloy formation occurs. This is evident by the AES uptake curves, the Al AES line shape change, the multilayer desorption kinetics, and the (v'3Xv'3)R30° LEED pattern, which is stable over a wide coverage range. This pattern is clearly interpretable in terms of the plane of the Al$_2$Ru intermetallic compound shown in Figure 4. The formation of this alloy requires that the Al atoms move into the Ru lattice. It is therefore understandable a highly activated process.

It is interesting to consider our results in light of the bulk phase diagram for the Al/Ru system. Since our system involves a small amount of Al and a large amount of Ru, the thermodynamically preferred structure would be a mixture of a nearly pure Ru phase and the compound AlRu. The bulk compound Al$_2$Ru is only thermodynamically preferred at concentrations exceeding ~50 atom % Al, and less than ~75%. At higher Al concentrations, Al$_3$Ru, Al$_6$Ru, and higher compounds appear (in mixtures of segregated phases). Thus, when we observe the Al$_2$Ru compound after annealing to 1170 K, the system may not have yet reached its equilibrium structure. The fact that Al$_2$Ru appears over such a broad coverage range may be due to the fact that it is kinetically prohibited from converting to the surface Al/Ru alloy that is more stable than bulk Al$_2$Ru. The melting point of these compounds increases with decreasing Al content from ~950 K for the Al richest phase, to ~2300 K for Al$_2$Ru. Since a substantial fraction (~1/3) of the melting temperature is normally required for alloy growth in a reasonable time scale, we should not be surprised that AlRu is not formed here at 1170 K. On the other hand, Al$_3$Ru$_2$ and Al$_3$Ru melt as a eutectic at only ~1570 K, and Al$_3$Ru was often observed to form rapidly from solid Al/Ru, upon cooling below ~1270 K. This testifies to the ease of formation of Al$_2$Ru, which would explain why it is seen here.

Our Al thermal desorption data show the decomposition of a multilayer alloy (Al$_3$Ru$_2$) with an activation energy of ~88 kcal/mol at ~1300 K. Since there is typically no excess activation energy beyond the thermodynamic barrier for such atomic desorption steps, this energy approximates the reaction enthalpy for the process: Al$_2$Ru$_2$(solid) $\rightarrow$ Al(gas) + xRu(solid). Since the sublimation energy of Al is ~74 kcal/mol at this temperature, we can approximate the heat of formation of the alloy as ~88 - 74 = ~14 kcal/mol of Al. This value probably refers to either bulk Al$_3$Ru or Al$_2$Ru. The first Al$_2$Ru monolayer has an activation energy for desorption that is ~10 kcal/mol larger (see above), reflecting a heat of formation of about ~24 kcal/mol. To our knowledge, no other quantitative thermodynamic data exist for these alloys.
Interaction of CO with Al/Ru(0001) Surfaces

It is certainly clear that the structure of the Al/Ru interface greatly influences the way in which Al modifies the chemisorption of CO on Ru(0001). For the annealed surface where Al/Ru alloy formation occurs, the Al sits within the topmost Ru layer. In this situation, the interaction of CO with Ru is only weakly effected, as seen in Figure 6. At $\theta_{Al} \geq 0.67$, the absolute CO coverage is reduced to 0.39-0.45, which is close to the value of $1/3$ expected if each Ru atom in the structural model of Figure 4 adsorbs one CO molecule. These Ru atoms are surrounded by Al neighbors in the topmost plane and therefore might experience significant electronic influences. These, if they exist, are not strongly manifested in the CO desorption behavior. The well-known CO–CO lateral repulsions would be weak for CO adsorbed on Ru atoms in the geometry of Figure 4 but very strong at CO coverages above $1/3$, which exist on the clean surface. This coverage dependence appears to be as important in CO TDS as any directly Al-related electronic influence in the alloy. Thus, Al seems fairly close to an ideal diluting agent in this alloy, replacing Ru atoms in the topmost atomic layer, without strongly affecting the nature of the Ru–CO chemisorption bond. The lack of electronic influence of Al upon its neighboring Ru atoms, at least as reflected in the CO–TDS here, is rather surprising.

On the other hand, on the unannealed interface when Al adatoms sit on top of the Ru(0001) surface, they induce a very marked change in the CO chemisorption behavior. At high coverages, they eventually mask the surface completely from chemisorbing CO. This is due to the growth of an Al(111) film. No CO will adsorb on Al at 300 K. In addition, a new, very strongly adsorbed state of CO ($\gamma$) appears at low coverages of Al. This state desorbs at about 900 K, compared to about 450 K from clean Ru(0001). This difference reflects a doubling in the activation energy for CO desorption. This state reaches a maximum coverage $\theta_{CO} \approx 0.33$ at $\theta_{Al} \approx 0.67$ (Figure 7). This would suggest that two Al atoms (and a single Ru surface atom) are needed for each CO molecule in the $\gamma$ state. The nonlinear increase in the coverage of this $\gamma$ state with Al coverage for $\theta_{Al} < 0.2$ would also be consistent with such a picture.

We should point out that the CO exposure of 12 langmuirs used for Figures 5–8 was proven to be sufficient for saturation on the clean Ru(0001) surface. It is possible that the CO sticking probability could be reduced by Al, so that these data do not necessarily reflect saturation coverages of CO for the Al-dosed surfaces. However, a CO exposure that was 2.5 times larger than those reported here gave no significant increase in the CO TDS peak area for the one case of an unannealed Al overlayer of coverage $\theta_{Al} \approx 0.7$. This indicates that many if not all of these experiments were for saturation CO coverages.

Very similar high-temperature CO desorption states are seen for Mn overlayers on Ru(0001).22 Clear isotopic scrambling in the case of Mn addition suggested that this CO desorption peak may be due to the recombination of dissociated CO: $\text{C}_2 + \text{O}_2 \rightarrow \text{CO}$. However, UPS data suggested that the CO was still molecular.22 The $\text{C} + \text{O}$ recombination reaction on clean Ru surfaces typically gives CO desorption peaks in the range 550–650 K, unless the carbon is in a graphitic form.23 At this point, we can only speculate on the nature of this $\gamma$ state. The Al–O bond can be very strong, as evidenced by the high stability of Al$_2$O$_3$. One can therefore imagine that the oxygen end of the CO molecule is somehow attached to the nearby Al adatoms. In any case, we envision a very direct interaction between CO and the Al adatoms. The small difference in Pauling's electronegativities for Al (1.61) and Ru (2.2) suggests the possibility of a weak electron charge transfer from Al to Ru. This is, however, expected to be much smaller than for cases such as K on Ru(0001), where substantial charge transfer results in a marked indirect electronic influences on the Ru and consequent large changes in CO desorption behavior.24 The smaller charge transfer expected here requires that a more direct model for the Al–CO interaction be used to explain the very dramatic influences of Al upon CO chemisorption.

Very recently, Rao and co-workers have studied the adsorption of CO on Al-dosed Ni and Cu surfaces.25 They, too, found a very strong influence of Al upon CO adsorption, evidenced both by a change in the valence energy levels and by a drastically reduced $\text{C}–\text{O}$ stretch frequency. They attributed this to an Al-induced precursor to dissociation and observed CO dissociation by 300 K. They did not comment on the thermal history of their Al overlayers but mentioned that alloy formation had already occurred. They developed a molecular-orbital picture of the Al effect by extended Hückel calculations of Cu$_3$Al–CO clusters. Their picture involved Al bonding to the carbon end of the CO molecule via its $\sigma$ orbital, coupled with Cu–CO interactions via the $1\pi$ orbital. Similarly, Chen and co-workers, in the accompanying paper, observe an EELS peak at 1370–1430 cm$^{-1}$ for CO on Ni/Al and assign this, for a number of reasons, to a $\text{Ni}_2$–C–O–Al, species which is a precursor to CO dissociation. In that case, the species dissociated completely between 450 and 700 K. No $\text{C} + \text{O}$ recombative desorption was seen by them at maximum temperature (700 K). Given the similarities between Ni and Ru with respect to CO chemisorption, we propose a similar mechanism for the interaction of CO with Al adatoms on Ru(0001). Thus, we envision the O end of adsorbed CO being attracted to the Al adatom and forming a bond which eventually leads to CO dissociation. We thus tentatively assign the 900 K $\gamma$-desorption state for CO to the recombinative desorption of $\text{C} + \text{O}$. This occurs at a higher temperature than observed on clean Ru(0001), which is at about 600 K, since now the oxygen and/or carbon adatoms are stabilized by interactions with Al.

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