Ru3(CO)12 Adsorption and Decomposition on TiO2

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Triruthenium dodecacarbonyl (Ru3(CO)12) adsorption and decomposition on titania (TiO2) were studied using infrared reflection absorption spectroscopy, temperature-programmed desorption, Auger electron spectroscopy, and scanning tunneling microscopy. It was found that the vapor-deposited cluster adsorbs with the Ru3 plane oriented normal to the surface. The clusters form an amorphous layer at 90 K, order at 195 K, and begin to decompose in a vacuum at ca. 250 K. The clusters decompose in two stages, with complete decomposition occurring above 600 K. The clusters are highly dispersed on the surface and decompose cleanly to form small ruthenium clusters up to 3 nm across and single atom rows up to 20 nm long.

Introduction

Metal carbonyls are important as precursors in catalysis and thin film technologies; thus, their surface chemistry is of fundamental and practical interest. The adsorption and decomposition in ultrahigh vacuum (UHV) of metal carbonyls on various surfaces have been the subject of several recent investigations (refs 1–4 and references therein). While their decomposition to metal clusters for heterogeneous catalysts (both mono- and bimetallic) has been the subject of numerous studies (see for example ref 5), it is only recently that metal carbonyls have been used as sources for the deposition of ultrathin oxide and/or metal films on semiconductors and metals.6 Some metal carbonyls are sufficiently volatile5 such that introduction into a UHV chamber is practical via an effusion cell. The pressure during the deposition (10−8–10−9 Torr) favors decarbonylation for certain systems, allowing the deposition of virtually carbon-free, highly dispersed metal clusters. This approach has recently been used to produce epitaxial films of RuO2 by dosing Ru3(CO)12 onto a heated TiO2(110) substrate under oxygen ambient.8

Ruthenium and ruthenia/titania composites are of interest for a variety of fundamental and practical reasons. Ruthenium is known to be active for low-temperature methane coupling9 and is active for CO and CO2 methanation, particularly when partially oxidized on titania clusters. This approach has recently been used to produce a variety of non-crystalline catalysts (both mono- and bimetallic) that show activity for CO2 methanation (TPD) indicated that the parent cluster is physisorbed on the titania surface. Bridges was reported. Temperature-programmed desorption (TPD) indicated that the parent cluster is physisorbed on the titania surface. It was found that the vapor-deposited cluster adsorbs with the Ru3 plane oriented normal to the surface. The clusters form an amorphous layer at 90 K, order at 195 K, and begin to decompose in a vacuum at ca. 250 K. The clusters decompose in two stages, with complete decomposition occurring above 600 K. The clusters are highly dispersed on the surface and decompose cleanly to form small ruthenium clusters up to 3 nm across and single atom rows up to 20 nm long.


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at room temperature and begins to decompose via CO evolution at 363 K. Extended X-ray absorption fine structure (EXAFS) and infrared data suggest the formation of \([\text{Ru}_3(\text{CO})_6(\mu-\text{OTi})_3]\) following an anneal to 473 K.\(^{17}\) This system serves as the benchmark for comparison of the present study with previous work.

Here, we report the use of infrared reflection absorption spectroscopy (IRAS) and TPD to study the adsorption and decomposition of Ru\(_3\)(CO)\(_{12}\) on TiO\(_2\) and the potential of this carbonyl precursor as a metal source for synthesizing thin films. Scanning tunneling microscopy (STM) of a TiO\(_2\)-(110) single crystal exposed to Ru\(_3\)(CO)\(_{12}\) vapor was used to acquire images before and after heat treatment at 573 K in an effort to develop a more complete picture of the decomposition process.

**Experimental Section**

The spectroscopic portion of this study was performed in a UHV chamber (base pressure less than \(2 \times 10^{-10}\) Torr) equipped with an Auger electron gun and cylindrical mirror analyzer (Perkin-Elmer), a quadrupole mass analyzer (QMS, UTI Instruments), a low-energy electron diffraction (LEED, Perkin-Elmer) spectrometer, and an infrared cell separated from the main chamber by a two-stage sliding seal. This apparatus has been described in detail elsewhere.\(^{18,19}\) The main chamber is also fitted with an effusion cell doser for the introduction of metal carbonyls or other solids with suitable vapor pressures. The doser is constructed of a perforated tantalum foil (H. Cross Co.) pocket mounted inside a UHV stainless steel tube and held in place with threaded rods. The doser is isolated from the main analysis chamber by a gate valve and can be evacuated independently of the main chamber and the infrared cell through an attached needle valve. This construction allows for the evacuation of ambient atmosphere without significant contamination of the UHV system. The doser's position on the main chamber also allows for the sample to be protected from contamination by insertion into the IR cell when the gate valve is initially opened. Using this configuration, outgassing of the doser could be accomplished independent of the sample.

The IRAS cell is fitted with flange-mounted CaF\(_2\) windows in the infrared beam path. The optics and windows are aligned such that the angle of incidence is 85° from surface normal, an ideal angle for IRAS.\(^{20}\) The infrared spectrometer used for data collection is a Mattson Cygnus 100 in single-beam mode using an MCT detector. All spectra collected in this study are averages of 512 scans at 4 cm\(^{-1}\) resolution.

The sample consists of a Mo(110) single crystal (Single Crystal Limited) that is mounted on the sample probe with a tantalum wire loop spot-welded around the edge of the sample and a type C thermocouple (wire supplied by H. Cross Co.) spot-welded to the back. This mount allows for resistive heating to 1500 K and liquid nitrogen cooling to 90 K. The Mo disk was cleaned by alternating annealing at 800 K in \(5 \times 10^{-4}\) Torr O\(_2\) and electron beam heating to 2000 K until no carbon or oxygen was observed using Auger electron spectroscopy (AES). The Ti doser was constructed by wrapping titanium wire (99.99+%, Goodfellow) around a tungsten wire loop (H. Cross Co.) pocket mounted inside a UHV stainless steel tube and held in place with a tungsten wire loop spot-welded around the edge of the sample and a type C thermocouple (wire supplied by H. Cross Co.) spot-welded to the back. This mount allows for resistive heating to 1500 K and liquid nitrogen cooling to 90 K. The sample was cleaned by alternating annealing at 800 K in \(5 \times 10^{-4}\) Torr O\(_2\) and electron beam heating to 2000 K until no carbon or oxygen was observed using Auger electron spectroscopy (AES). The Ti doser was constructed by wrapping titanium wire (99.99+% Goodfellow) around a tungsten wire loop (H. Cross Co.) that could be heated resistively. The doser was outgassed thoroughly by resistive heating prior to use. Oxygen (99.99%, Botco, Bryan, TX) and carbon monoxide (99.99%, Matheson Gas Products) were further purified by fractional condensation and transferred to glass bulbs. The CO bulb was left immersed in liquid nitrogen during experiments in order to condense volatile metal carbonyls that are typically formed when CO comes in contact with the steel.

gas manifold. Ru$_3$(CO)$_{12}$ (99%, Strem Chemicals, Inc.) was introduced into the effusion doser as received.

The titanium oxide thin films were produced by evaporation of titanium metal onto the Mo(110) crystal at 650 K in a background of $5 \times 10^{-6}$ Torr O$_2$. The films were annealed to 800 K in this oxygen background in order to ensure full oxidation and to eliminate adventitious carbon that was occasionally found in the films prior to annealing. Details of the film synthesis can be found elsewhere$^{21}$ essentially, these films are the rutile phase with a preponderance of (110) facets. Ru$_3$(CO)$_{12}$ was then dosed on the films at 90 K at a number of exposures; the exposure pressure for the carbonyl species was typically $1.8 \times 10^{-9}$ Torr.

IRAS and TPD were performed on the samples prior to decarbonylation, and AES was carried out afterward. TPD data were collected from 100 to 800 K at 28 atomic mass units and 1 K steps. AES was collected from 20 to 600 eV at 3 kV beam voltage.

Because Ru remained on the surface after the decomposition of Ru$_3$(CO)$_{12}$, the resulting composite films were evaporated from the sample by an e-beam flash to 2000 K. This procedure produces a clean Mo(110) substrate upon which a new titania film could be synthesized.

The imaging portion of this study was performed in a combined high-pressure cell/multitechnique UHV analysis chamber (base pressure less than $2 \times 10^{-10}$ Torr) that is equipped with a double-pass cylindrical mirror analyzer for AES and XPS, LEED optics (Perkin-Elmer), a QMS (UTI Instruments), and a UHV scanning tunneling microscope (Omicron). The apparatus consists of four main sections: a high-pressure cell, a surface analysis chamber, a sample preparation chamber, and a STM chamber; details are available elsewhere.$^{22}$

A Type C thermocouple (wire provided by H. Cross Co.) was attached to the edge of a TiO$_2$(110) crystal (Commercial Crystal Laboratories) using high-temperature ceramic adhesive (AREMCO 571). The thermocouple was used to measure the surface temperature and to calibrate a pyrometer (OMEGA OS3700) prior to its disconnection for the STM measurements. The pyrometer was then used to measure the temperature in subsequent annealing experiments. The crystal was prepared for experiments by alternating argon ion sputtering with high-temperature (1000 K and higher) annealing. This cleaning procedure has been described in detail elsewhere.$^{23}$ Following cleaning, the sample was introduced into the high-pressure cell to which the Ru$_3$(CO)$_{12}$ effusion cell was attached. After exposure to the cluster vapor, the sample was removed to the vacuum chamber in order to conduct the annealing and STM experiments.

**Results and Discussion**

Figure 1 shows the carbonyl stretching region of the IRAS spectrum of Ru$_3$(CO)$_{12}$ (exposure equal to 3 langmuir, where 1 langmuir $= 1 \times 10^{-6}$ Torr) adsorbed on TiO$_2$ at 90 K, as well as spectra acquired as the sample was heated. At 90 K, two broad features are apparent at 2084 and 2047 cm$^{-1}$. Both features exhibit a tail sloping to the low-energy side. As the temperature is increased, the feature at 2047 cm$^{-1}$ decreases slightly in intensity while the 2084 cm$^{-1}$ feature increases slightly in intensity, with the low-energy tail diminishing. Between 180 and 195 K, the spectrum transforms sharply in that a symmetric feature appears at 2029 cm$^{-1}$ with a small shoulder at 2041 cm$^{-1}$. The strong feature at 2084 cm$^{-1}$ also becomes more symmetric at this temperature. As the temperature is increased further, the entire spectrum red-shifts slightly and becomes broader and more asymmetric until no features are apparent at 295 K. This sample was then cooled to 90 K, and $1 \times 10^{-5}$ Torr CO was introduced; no absorption features were apparent at this temperature and pressure.

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These powdered samples show transmission IR features at 2140 cm$^{-1}$ (w) and 2085 cm$^{-1}$ (w) and a broad heterogeneous band with its maximum located around 2060 cm$^{-1}$ (s). There is also no agreement between the spectra of this study and that of CO adsorbed on metallic single crystals, such as CO/Ru(001), which have infrared absorption features at 2080 cm$^{-1}$ (w) and 2048 cm$^{-1}$ (s). Furthermore, a significant breakdown in symmetry due to strong adsorbate–support interactions is unlikely, as the increased spectral complexity expected to result from such interactions does not appear. See, for example, the infrared spectra of Ru$_2$Os(CO)$_{12}$, RuOs$_2$(CO)$_{12}$, FeRu$_2$(CO)$_{12}$, and Fe$_2$Ru(CO)$_{12}$ systems in which the molecular symmetry has been reduced from D$_{3d}$ to C$_{2v}$. A similar symmetry reduction would be consistent for Ru$_3$(CO)$_{12}$ oriented with the Ru$_3$ plane normal to the substrate, assuming there is a sufficiently strong adsorbate–substrate interaction.

Considering these points, the IRAS spectra are most consistent with random initial adsorption (indicated by the broad heterogeneous features at low temperature) with subsequent ordering between 180 and 195 K into a geometry where the Ru$_3$ plane is perpendicular to the surface. As previously discussed, only equatorial vibrational modes should be observed when the Ru$_3$ plane is parallel to the surface. Comparison of the surface spectra to the solution spectra yields similar peak amplitude and relative position, with the notable exception that the axial mode observed in the solution phase is invisible in IRAS. IRAS data cannot be used to determine how individual ruthenium atoms are oriented with respect to the surface, nor can IRAS show whether there is a preferred molecular orientation with respect to the substrate atomic rows; however, the orientation of the Ru$_3$ plane with respect to the surface plane is clear.

These results contrast with those in which Ru$_3$(CO)$_{12}$ was adsorbed onto a titania powder by wet impregnation. The bands that Asakura et al. assign to physisorbed Ru$_3$(CO)$_{12}$ nearly match the two most intense bands of the sample dissolved in hexane (2065 cm$^{-1}$ (s) and 2030 cm$^{-1}$ (s)), while those features observed following a heat treatment at 473 K (2139 cm$^{-1}$ (w), 2081 cm$^{-1}$ (s), and 2009 cm$^{-1}$ (s), as shown in the line spectrum overlay in Figure 4) are somewhat different than those observed in the thin film sample of this study (2085 cm$^{-1}$ (s), 2041 cm$^{-1}$ (w), and 2029 cm$^{-1}$ (w)). It is evident from the IRAS data alone that the thin film sample and the powdered sample are not entirely analogous. It is unclear whether these differences are due to the phase of the substrate (the powder is expected to contain substantially more anatase than the thin film), the nature of the deposition method, or both. In any case, since the infrared spectra of the sample formed by wet impregnation is isotropic, no direct molecular orientation comparison can be made: the variations in peak positions and relative intensities between the two methods are the primary evidence that the sample formed by vapor deposition differs from that formed by wet impregnation. Thus, the evidence of this work, which indicates a perpendicular molecular orientation, need not be considered contradictory to that of Asakura et al., which suggests a parallel orientation.

Finally, following elimination of the IRAS signal at 295 K, no IRAS features are seen upon introduction of CO at...
90 K. Two possible reasons for this result are either complete cluster desorption or decomposition of the cluster in such a way that few ruthenium sites are available for CO adsorption (due to insertion and oxidation of ruthenium into the titania lattice). The TPD and AES results reported here together with the results of Rizzi et al.\textsuperscript{14} suggest that the latter is the case.

Figure 5 shows CO TPD data for several Ru\textsubscript{3}(CO)\textsubscript{12} exposures. Most notably, CO evolution occurs in two stages at all coverages. For the 0.5 langmuir exposure, the first desorption feature appears at 300 K, followed by a second at 500 K. At this low coverage, the peak areas are approximately identical. As coverage is increased, a number of things occur. First, the second desorption peak increases substantially with respect to the first while shifting to lower temperature (360 K at 5 langmuir). Also, at the higher coverages two new features emerge: the first, centered at about 150 K, is attributed to multilayer desorption, while the second appears around 610 K.

The assignment of the TPD decomposition features is aided substantially by the temperature-dependent IRAS spectra discussed above. Note that at 295 K there are no features in the IRAS spectrum that correspond to the TPD desorption feature at 300 K (as marked in Figure 5). However, the TPD data show that the CO does not fully desorb from the surface until 500 K or higher; a substantial amount of CO remains on the surface after IRAS no longer shows any evidence of it. Since the IRAS features have been assigned to the equatorial carbonyl vibrational modes of the cluster with the Ru\textsubscript{3} plane oriented perpendicular to the surface, it follows that these modes disappear with the initial carbonyl elimination from the cluster. This does not necessarily indicate that exclusively equatorial carbonyl groups are desorbing; the equatorial vibrational modes would also disappear upon dissociation of Ru—Ru bonds, resulting in the demolition of the original cluster. Furthermore, since no other bands are visible after the first stage of the decomposition, it follows that the remaining surface CO is bound tangential to the surface plane, much like the axial CO molecules in the adsorbed cluster. It has been suggested previously by Asakura et al.\textsuperscript{17} that the initial desorption leaves a ruthenium polynuclear subcarbonyl species bound to the surface, that is, Ru\textsubscript{3}(CO)\textsubscript{6}(\mu-O\textsubscript{2}Ti)\textsubscript{3}. While this could be a plausible interpretation of the current data, other possibilities must be considered in light of the previously discussed discrepancies between the vapor-deposited and wet-impregnated samples. One such possibility could be the formation...
of single-metal subcarbonyl species, such as Ru(CO)\textsubscript{2} and Ru(CO)\textsubscript{3}. These species have been reported on TiO\textsubscript{2} previously\textsuperscript{25} and could account for the increased intensity of the high-temperature decomposition peak with respect to the low-temperature peak as the cluster coverage is increased. In effect, initial decomposition of the adsorbed cluster at low coverage would produce 3Ru(CO)\textsubscript{2} + 6CO, resulting in the nearly equal CO TPD peak areas during cluster decomposition. As coverage increases, greater interaction between Ru(CO)\textsubscript{2} and desorbing carbonyls could result in the formation of some Ru(CO)\textsubscript{3} with a stoichiometry of \(X\)Ru(CO)\textsubscript{3} + (3 - \(X\))Ru(CO)\textsubscript{2} + (6 - \(X\))CO, where \(X\) ranges from 0 to 3 and increases with coverage. This explanation allows for up to a 3:1 peak area ratio between the second and first decomposition features at high coverage, which is consistent with the TPD results. As both of these single-metal ruthenium subcarbonyl species could be planar, their formation would be consistent with the IRAS data assuming that their molecular planes are mostly parallel to the surface.

AES verifies that the cluster decomposition is complete and clean at 800 K. Figure 6 shows the Auger of the TiO\textsubscript{2}/Mo(110) system before and after 5 langmuir Ru\textsubscript{3}(CO)\textsubscript{12} exposure and TPD to 800 K. The adsorbed ruthenium is plainly seen (259 eV), but an unfortunate coincidence of the ruthenium and carbon features requires comparison to the published peak shapes.\textsuperscript{29} The ratio of the positive amplitude of the derivative feature to the total amplitude is approximated as a linear combination of the ratios found for the pure elements. The relative concentration of ruthenium can then be found by using the usual elemental composition equation, thereby factoring in the Auger sensitivities for the respective features. This computation indicates that approximately 90% clean ruthenium remains on the surface following Ru\textsubscript{3}(CO)\textsubscript{12} decomposition, assuming no corrections are necessary to compensate for slight variations in the electronic structures of the adsorbed species.

Regardless of the differences between the decomposition characteristics of the vapor-deposited sample and those of the wet-impregnated sample, the vapor deposition method clearly results in highly dispersed ruthenium clusters on the rutile surface. Figure 7 shows a large field STM image of the clean TiO\textsubscript{2}(110) after exposure to Ru\textsubscript{3}(CO)\textsubscript{12} and vacuum annealing at 600 K for 60 s. The surface is covered with clusters of dimensions up to 3 nm in diameter. While there is some agglomeration at step edges, it is not noticeably more abundant than clustering on terraces. Also visible in the image are a number of bright "stripes" of atoms parallel to the [001] surface vector. Finally, there are single bright atomic spots, a phenomenon previously assigned to interstitial titanium ions moving from the bulk to the surface upon annealing, albeit at somewhat higher temperatures than here.\textsuperscript{23} Due to the chemical insensitivity of STM, it cannot be conclusively determined whether the stripes are due entirely to interstitial transport, ruthenium atoms, or some combination thereof.

An expanded image of the same surface is shown in Figure 8. In the center of the image, a cluster of 1.3 nm diameter and 0.2 nm thickness is outlined (A), a size corresponding to a ruthenium cluster numbering on the

order of 14–20 atoms. Just below that cluster, there is a structure (B) which appears as three bright spots that are collinear with the TiO2 [001] vector directly atop features previously assigned to exposed rows of titanium ions in the rutile structure. These spots are flanked on each side by slightly dimmer spots that are atop the dark rows previously assigned to the TiO2 bridging oxygen.30 While it is tempting to assign this structure to three adjacent Ru(CO)2 units arising from the decomposition of a single trinuclear cluster, it must be stressed that structures such as these are not common; longer stripes or larger multiclus-ter features make up the preponderance of the surface features (as shown in Figure 7). Further study is required to determine whether these are in fact the result of decomposed single trinuclear clusters or simply a fortuitous collection of interstitials; however, such features are consistent with the decomposition scheme in which perpendicularly adsorbed molecular Ru3(CO)12 decomposes into RAS-invisible Ru(CO)2 collinear with the [001] surface vector, which at higher temperatures further decomposes to form three ruthenium atoms on the surface (Figure 9).

The STM evidence provides another indirect means to compare vapor-deposited samples to wet-impregnated ones. While the clusters of this study are at most a few tens of atoms in size, EXAFS studies performed on wet-impregnated samples indicate high Ru–Ru coordination and therefore larger three-dimensional particles than those shown in the present work.31

Figure 8. Expanded view of Figure 7. Two features (A and B) discussed in the text are circled. Feature A is accompanied by a cross section showing a cluster thickness of 0.2 nm, which is on the order of a single atomic layer.

Conclusions

We have developed, through a combination of techniques, a comprehensive proposal for the mechanism by which vapor-deposited Ru₃(CO)₁₂ decomposes on titania surfaces. It is found by IRAS that deposition at low temperature gives rise to a disordered film that orders as the temperature increases into an adsorbed system in which largely unperturbed clusters are oriented with the Ru₃ plane perpendicular to the surface plane. These clusters begin to decompose at 250 K and are invisible in IRAS starting from 295 K. TPD results confirm that decomposition occurs in two stages and is complete at 600 K. This result is consistent with the formation of planar single-metal ruthenium subcarbonyls adsorbed parallel to the surface which then further decompose to form ruthenium aggregates. STM results show clusters up to 3 nm in diameter located on both terraces and step edges as well as rows of atoms oriented atop the [001] rows of titanium ions.

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