Particulate Cu on Ordered Al₂O₃: Reactions with Nitric Oxide and Carbon Monoxide

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The growth of small Cu particles, prepared by vacuum vapor deposition, on Al₂O₃ films on Mo(100) has been studied in the 80-800 K substrate temperature range with Auger electron spectroscopy (AES) and temperature-programmed desorption (TPD). A model based on Auger measurements has been utilized to examine the number density and the average size of the Cu particles on Al₂O₃. Nitric oxide decomposition on the Cu particles has been further investigated using TPD and high-resolution electron energy loss spectroscopy (HREELS). TPD and HREELS data clearly show that a fraction of the NO molecules react with the Cu particles to produce gaseous N₂ and N₂O in the 90-250 K temperature range. The formation of N₂ at 770 K is also evident and is due to the recombination of adsorbed N atoms from NO dissociation. The effects of retained oxygen, adsorption temperature, and particle size on the production of high-temperature N₂ have been examined. The reaction between nitric oxide and carbon monoxide has also been studied. The results show that, besides the N₂ and N₂O products arising from NO decomposition, a small quantity of CO₂ is produced by the reaction between adsorbed CO and adsorbed oxygen.

Introduction

Small supported metal particles have become an area of intense research interest in recent years due primarily to their importance in heterogenous catalysis. Very small metal particles and clusters containing from a few to thousands of atoms often exhibit physical and chemical properties different from their bulk counterparts. Several previous studies have demonstrated that small supported metal particles can be reproducibly prepared in a controlled way by vapor deposition of the parent metal onto planar supports in an ultrahigh-vacuum environment. The catalytic properties of these particles can then be addressed systematically with respect to particle size, morphology, and the influence of supports.

Recently, we have undertaken an initiative to study small metal particles supported on planar oxide substrates using surface-sensitive techniques. This article reports a study of the CO/NO reaction carried out on Al₂O₃-supported Cu particles. This work focuses on the effects of Cu particle size on the CO/NO reaction chemistry. Copper is an active component in many catalytic reactions, such as CO oxidation and NO reduction. There is a recent, growing interest in the catalytic decomposition of nitric oxide over Cu-containing zeolite due to environmental concerns.

Because many oxide supports used in catalysis are bulk insulators or wide gap semiconductors, problems with surface charging are encountered with these materials during charged particle measurements. Various approaches, such as the use of a neutralization electron gun, have circumvented these difficulties. In particular, the successful synthesis of epitaxial ultrathin oxide films has offered new opportunities and avenues to study the surface chemistry of these materials using surface science techniques.

Our strategy to study supported metal particles involves the following procedure: (1) preparation of ultrathin oxide films on a single-crystal refractory metal surface [the use of a refractory metal with an appropriate lattice confinement provides a thermally stable substrate for heteroepitaxy of single-crystal oxide films], (2) deposition of oxide precursor metals onto the refractory metal surface in a controlled oxygen environment, and (3) vapor deposition of metals of catalytic interest onto the films. This approach allows us to use an assortment of surface-sensitive electron spectroscopies without difficulties associated with surface charging and to prepare metal particles in a controlled, reproducible way. In this study, we exploit our early success in preparing highly ordered oxide films to study CO/NO surface chemistry on particulate Cu deposits synthesized on planar, epitaxial Al₂O₃ films.

Experimental Section

The experiments were carried out utilizing an ultrahigh-vacuum (UHV) system, described elsewhere, with capabilities for high-resolution electron energy loss spectroscopy (HREELS), Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and temperature-programmed desorption (TPD) and facilities for sample heating and cooling. The refractory metal Mo(110) was chosen as a substrate for preparing the thin Al₂O₃ films. The crystal cleaning and handling can be found elsewhere. Sample temperatures were monitored with a pair of W-5% Re/W-26% Re thermocouple wires spot-welded to the edge of the rear surface.

Thin Al₂O₃ films were prepared by exposing Mo(110) to Al vapor in a controlled oxygen atmosphere. Aluminum deposition was performed via thermal evaporation of high-purity wires inserted into a small cylindrical alumina tube. The cylinder was then tightly fitted into a spiral tungsten filament whose ends were spot-welded to two support electrodes. The assembly was surrounded by a cylindrical shroud, open at one end and capped at the other. The source was initially thoroughly outgassed, and the aluminum wires were melted prior to use. The stable flux, obtained by applying constant power to the filament, was monitored by carrying out a series of TPD spectra after each deposition onto the Mo(110) substrate. This homemade crucible source was capable of delivering a stable and reproducible flux over a period of several months under UHV operation conditions.

Copper was evaporated from a source containing a high-purity wire tightly wrapped around a tungsten filament. The source, thoroughly outgassed before use, was operated at constant power for each deposition.

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Particulate Cu on Ordered Al₂O₃ in oxygen ambient to improve their crystalline quality. The spectra were acquired at \( E_p = 2.0 \text{ keV} \) and at a sample current of 5 \( \mu \text{A} \).

Spectroscopic grade \(^{15}\text{NO} \) (\(^{15}\text{N}, \text{98.98\%} \)) and CO (99.99\%) were used without further purification in the adsorption studies. The reactants were introduced via a gas nozzle doser, which was directed to the crystal surface and at a distance of approximately 0.5 cm from the crystal face.

The temperature-programmed description spectra were obtained at a linear heating rate of 5–10 K/s using a quadrupole mass spectrometer. Auger measurements were carried out using an electron beam with an impact energy of 2 keV and at a sample current of typically 5 \( \mu \text{A} \). The HREELS spectra were acquired in the scattering compartment of a two-tiered chamber.\(^{12-14} \) The HREELS data were collected in a specular scattering geometry with an incident angle of the electron beam of 60° about the surface normal.

**Results and Discussion**

**Preparation and Characterization of the Al₂O₃ Films.**

Thin Al₂O₃ films were grown at room temperature on a freshly cleaned Mo(110) surface. The growth of the films was controlled at a rate of approximately one-half aluminum equivalent monolayer per minute. The background pressure of oxygen was \( 7 \times 10^{-7} \text{Torr} \) during film growth. The films were annealed to 1200 K in oxygen ambient to improve their crystalline quality. Shown in Figure 1 are Auger spectra acquired following film synthesis at two representative film thicknesses: (a) \( d_{\text{Al2O3}} = 4.4 \text{ Å} \) and (b) \( d_{\text{Al2O3}} = 20.0 \text{ Å} \). The thickness of the \( d_{\text{Al2O3}} = 4.4 \text{ Å} \) film was calculated from the Auger intensity ratio of the Al\(^{3+} \)(LVV) and Mo(MNN) peaks using the following equation:

\[
\frac{I_{\text{Al}^{3+}}}{I_{\text{Mo}}} = \frac{\rho_{\text{Al}^{3+}}}{\rho_{\text{Mo}}} \left( 1 - e^{-d_{\text{Al}^{3+}}/\lambda_{\text{Al}}} \right) / \left( 1 - e^{-d_{\text{Al}^{3+}}/\lambda_{\text{Mo}}} \right)
\]

The value of \( \rho_{\text{Al}^{3+}}/\rho_{\text{Mo}} \) was obtained from the standard Auger spectra of Al₂O₃ and Mo, respectively.\(^{16} \) The attenuation lengths, \( \lambda_{\text{Al}^{3+}} \) and \( \lambda_{\text{Mo}} \), were taken from the literature to be 3.7\(^{17} \) and 6.7 Å,\(^{18} \) respectively. The thickness of the thick film (\( d_{\text{Al2O3}} = 20.0 \text{ Å} \)) was estimated by extrapolating the value of the thin film based on evaporation time and constant aluminum flux.

It is seen in Figure 1 that there is no indication of the presence of a metallic Al\(^{3+} \) feature at 68 eV. The predominant spectral features are the Al\(^{3+} \)(LVV) transitions at \( \sim 54 \text{ eV} \) and the O(KLL) transition at \( \sim 500 \text{ eV} \). The spectral features in the

![Figure 1. Auger spectra of Al₂O₃ films grown on Mo(110): (a) \( d_{\text{Al2O3}} = 4.4 \text{ Å} \) and (b) \( d_{\text{Al2O3}} = 20.0 \text{ Å} \). The films were annealed to 1200 K in oxygen ambient to improve their crystalline quality. The spectra were acquired at \( E_p = 2.0 \text{ keV} \) and at a sample current of 5 \( \mu \text{A} \).](image)

![Figure 2. HREELS spectra of Al₂O₃ films grown on Mo(110): (a) \( d_{\text{Al2O3}} = 4.4 \text{ Å} \) and (b) \( d_{\text{Al2O3}} = 20.0 \text{ Å} \). The films were annealed to 1200 K in oxygen ambient to improve their crystalline quality. The spectra were acquired at \( E_p = 4.0 \text{ eV} \) and at the specularly reflected beam direction.](image)

100–250 eV kinetic energy range of spectrum a arise from the Mo substrate.

Structural studies of very thin Al₂O₃ films (\( d_{\text{Al2O3}} \leq 8 \text{ Å} \)) using LEED showed a complex pattern in which most diffraction spots can be interpreted as arising from electron multiple scattering at the interface. With an increase in film thickness, the multiple diffraction effects were attenuated. A simple hexagonal structure was seen at \( d_{\text{Al2O3}} \geq 15 \text{ Å} \) although the diffraction spots were not as sharp as those from multiple diffraction, indicating some degree of disorder in the thick films. The lattice periodicity derived from the LEED photographs relates closely to the O–O distance in bulk Al₂O₃. The observed hexagonal pattern can therefore be interpreted as due to the presence of an ordered, close-packed oxygen anion layer associated with either the (001) orientation of \( \alpha \)-Al₂O₃ or the (111) face of \( \gamma \)-Al₂O₃. A detailed structural analysis of the initial stage of epitaxy of Al₂O₃ films on a similar refractory metal substrate, Ta(110), has been given elsewhere.\(^{19} \)

The growth of Al₂O₃ films has been further examined using HREELS, as shown in Figure 2. The fundamental modes of the surface optical phonons (below 1000 cm\(^{-1} \) in frequency) and their multiples and combinations are evident in the spectra. The surface optical phonon losses of the thin film (spectrum a) are characterized by a two-mode pattern, whereas three modes of the phonon losses are typical for the thick film (spectrum b). These results are in a complete agreement with previous data in the literature.\(^{20-22} \) Frederick et al.\(^{24,25} \) have suggested that the appearance of the two phonon modes are characteristic of very thin Al₂O₃ films.

**Growth of Particulate Cu on Al₂O₃.**

The growth of particulate Cu deposits on these well-defined Al₂O₃ films has been studied in the 80–800 K substrate temperature range. The films utilized for supporting Cu particles were typically 20 Å thick and exhibited excellent thermal stability and chemical inertness toward adsorption. It has been reported\(^{26} \) that very thin Al₂O₃ films (\( d_{\text{Al2O3}} < 8 \text{ Å} \)) grown on Al substrates react with Ni deposits at elevated temperatures, causing diffusion of Ni into the substrate through defects in the Al₂O₃ film.

It has long been known\(^{1-3} \) that particulate metal deposits prepared at relative low substrate temperatures exhibit smaller average particle size and higher particle density than those prepared at higher temperatures; however, the low-temperature preparations are unstable and undergo a major change in morphology and size upon annealing or chemisorption. To
prepare thermally and chemically stable particles of catalytic interest, it is imperative to carry out the metal deposition at elevated substrate temperatures. A linear heating rate of 10 K/s was used.

Figure 3. TPD spectra of Cu following Cu deposition on Al₂O₃ films at various substrate temperatures. The Cu coverages (θCu = 1.0) for each spectrum were adjusted to be approximately the same. A linear heating rate of 10 K/s was used.

Figure 4. A family of TPD spectra of Cu deposited at Tₛ = 600 K as a function of equivalent monolayers, θCu: (a) 0.16, (b) 0.33, (c) 0.50, (d) 0.67, (e) 0.98, (f) 1.25, (g) 1.55, and (h) 2.09. The insert shows the heat of sublimation, derived from the leading edge analysis of the spectra, as a function of Cu coverage in equivalent monolayers. A linear heating rate of 10 K/s was used.

Figure 5. Auger intensity ratio of the Cu(LMM) peak to the O(KLL) peak versus the Cu coverage in equivalent monolayers. The solid line is a theoretical simulation based on the isotropic growth model, as discussed in the text. The number density of Cu particles, derived from a curve-fitting procedure, is 1.4 × 10¹¹ cm⁻². The average sizes of the Cu particles are inserted as vertical bars.

attributed to a decrease in the number of neighboring Cu atoms as the Cu particles become smaller.

The average size of the Cu particles can be estimated from Auger measurements. Figure 5 shows Auger intensity ratios of the Cu(LMM) peak to the O(KLL) peak versus Cu equivalent monolayers. Each data point was collected after a fresh deposition of Cu onto the clean Al₂O₃ surface at Tₛ = 600 K. The solid curve through the Auger data in Figure 5 represents a theoretical simulation based on a simple model described as follows: (1) Nucleation takes place homogeneously. (2) After an initial nucleation period, the number of particles remains constant until the stage where coalescence sets in. (3) The particle shape remains constant during growth. Using the algorithm formulated in the Appendix, the density of Cu particles, N, can be computed from a curve-fitting procedure. The calculated number of N = 1.4 × 10¹¹ cm⁻² compares favorably with those obtained by direct measurements with transmission electron microscopy (TEM); for the gold/mica system, N = (1.0–1.5) × 10¹¹ cm⁻² at Tₛ = 623 K. For
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Figure 6. Thermal desorption signals for m/e = 30, 31, and 46 from ¹⁵NO adsorbed on the Cu particles at 80 K versus ¹⁵NO exposure time, t; (a) t = 20 s, (b) t = 60 s, (c) t = 120 s, and (d) t = 300 s. The exposure at t = 640 s corresponds to saturation. θ_Cu is 0.67, corresponding to a cluster size of ~65 Å. A linear heating rate of 5 K/s was used.

The silver/amorphous carbon system, N = 1.0 × 10¹¹ cm⁻² at Tᵢ = 742 K.¹³ The average sizes of the Cu particles, derived from a curve-fitting procedure, are inserted as vertical bars in Figure 5.

Reactions of Nitric Oxide with Particulate Cu. The reaction of nitric oxide with well-characterized particulate Cu deposits grown on highly ordered Al₂O₃ films has been studied using TPD and HREELS. To differentiate N₂ molecules formed during reaction from background CO residual in the TPD, isotopically labeled nitric oxide, ¹⁵NO, was used in this study. Thermal desorption products from ¹⁵NO adsorbed on Cu particles at 80 K have been followed by monitoring several masses (m/e = 30, 31, 32, 46, and 47). θ_Cu was 0.67, corresponding to the cluster size of ~65 Å. Shown in Figure 6 are desorption signals for m/e = 30, 31, and 46 versus ¹⁵NO exposure. No desorption signals for m/e = 32 and 47 were observed in the 80–850 K temperature range, indicating the absence of gaseous O₂ and ¹⁵NO₂ products, respectively.

TPD spectra (m/e = 30) are characterized by the presence of two desorption states, designated as a β₁ state and a β₂ state, as indicated in Figure 6. The β₁ state at ~770 K can be easily explained as arising from the recombination of adsorbed ¹⁵N from dissociation of ¹⁵NO. The interpretation of the low-temperature state (β₂ state) is not so straightforward. While the β₁ peak tracks the m/e = 46 TPD peak as the ¹⁵NO exposure is varied, the difference in peak maxima by 16 K between the β₁ state and the desorption peak of the parent molecules (m/e = 31) is evident. The m/e = 46 TPD peaks arise from the desorption of ¹⁵N₂O. Since the m/e = 30 fragment in the cracking pattern of ¹⁵N₂O molecules, detected mass spectrometrically,³ is only 10% in intensity of that of m/e = 46, a portion of the β₁ peak must arise from ¹⁵N₂ production.

It follows then that adsorbed ¹⁵NO desorbs through two major pathways: a fraction of adsorbed ¹⁵NO molecules desorb associatively in the 90–250 K temperature range; the remaining molecules undergo dissociation to form adsorbed nitrogen and oxygen. The recombination of adsorbed ¹⁵NO and adsorbed ¹⁵N₂ forms ¹⁵N₂O at temperatures as low as 110 K. HREELS results described in the following sections further show that a ¹⁵N₂O species is present even at 80 K. The ¹⁵N₂ production is also evident in the 110–250 K temperature range. Finally, two adsorbed ¹⁵N atoms recombine and desorb at temperatures exceeding 700 K.

The chemistry of nitric oxide decomposition on Al₂O₃-supported Cu particles is summarized as follows:

\[
¹⁵\text{NO} \rightarrow ¹⁵\text{NO}
\]

\[
¹⁵\text{NO} + ¹⁵\text{N} + \text{O}_2 \rightarrow ¹⁵\text{N}_2 + ¹⁵\text{NO}
\]

\[
¹⁵\text{N} + ¹⁵\text{N} \rightarrow ¹⁵\text{N}_2
\]

where the subscript (a) denotes adsorbed species. It becomes obvious from the stoichiometry of the above reaction mechanism that the ¹⁵NO decomposition produces oxygen retained on the Cu particles. Figure 7 shows TPD spectra of Cu (m/e = 63.5) and of O₂ (m/e = 32), with desorption signals arising from the products of ¹⁵NO decomposition. O₂ is seen to desorb in the same temperature range as the desorption of Cu, indicating that the retained oxygen may dissolve into the Cu particles. The influence of the retained oxygen on the production of ¹⁵N₂ (β₁ state) will be addressed in detail in the following paragraphs.

Figure 8 shows the β₁ desorption peak ¹⁵N₂ versus the number of adsorption cycles. The experiments were carried out in a successive fashion without removal of the retained oxygen; ¹⁵NO exposures were the same for the three identical experimental runs. The integrated ¹⁵N₂ TPD area in the first experimental run is seen to be only one-third of that of the second. The ¹⁵N₂ yield then remained nearly constant in the successive experimental runs. This feature shows that the initially retained surface oxygen promotes the ¹⁵N₂ production significantly. The nature of the retained oxygen species and the state of Cu, namely, Cu⁺ or Cu₂⁺, are not clear at the present
Figure 8. The $\beta_3$ desorption peak of $^{15}$N$_2$ versus the number of adsorption cycles. $\theta_{Cu}$ was 0.67, corresponding to a cluster size of $\sim$65 Å. The experiments were carried out successively without removal of the retained oxygen; the $^{15}$NO exposures were the same for the three identical experimental runs. A linear heating rate of 5 K/s was used.

Figure 9. The $\beta_3$ desorption peak of $^{15}$N$_2$ obtained following $^{15}$NO exposure at three different adsorption temperatures: (a) $T_s = 80$ K, (b) $T_s = 150$ K, and (c) $T_s = 300$ K. $\theta_{Cu}$ was 0.67, corresponding to a cluster size of $\sim$65 Å. A linear heating rate of 5 K/s was used.

time. Further study utilizing techniques that probe the electronic states of Cu and oxygen is necessary to clarify these issues.

The influence of the substrate temperature, $T_s$, during adsorption on $^{15}$N$_2$ production ($\beta_2$ state) has also been examined. Shown in Figure 9 are the $\beta_2$ desorption peaks at three different substrate temperatures. The $^{15}$N$_2$ yield appears to maximize at $T_s = 150$ K. A decrease in $^{15}$N$_2$ production at $T_s = 300$ K can be attributed to a decrease in the sticking coefficient of $^{15}$NO at this elevated temperature.

Plotted in Figure 10 is the integrated $^{15}$N$_2$ TPD area ($\beta_2$ state) as a function of the Cu coverage in equivalent monolayers. The average sizes of the Cu particles also are indicated.

Figure 10. The integrated $^{15}$N$_2$ TPD area ($\beta_2$ state) as a function of the Cu coverage in equivalent monolayers. The average sizes of the Cu particles also are indicated.

Figure 11. HREELS spectra of (a) a clean Al$_2$O$_3$ film, $d_{AlO_2} = 8$ Å, and (b) Cu/Al$_2$O$_3$, $d_{AlO_2} = 8$ Å, $\theta_{Cu} = 2.7$, following a saturation exposure of $^{15}$NO at 80 K. The spectra were acquired using an electron beam with a primary energy of $E_p = 42$ eV and at the specularly reflected beam direction.

Recently, we have developed a new approach to the acquisition of HREELS data in order to circumvent the difficulties associated with these phonon losses. By utilizing a high-energy incident electron beam, this new approach enables the direct observation of relatively weak adsorbate features without serious interference from the intense multiple surface optical phonon losses.

The use of an electron beam with a high impact energy often produces a relatively low count rate in the elastic peak. Because of the low signal levels encountered in these HREELS measurements, an optimal Fourier filtering technique has been utilized to remove high-frequency random noise and spikes in the spectra. All HREELS spectra reported below have been smoothed using this Fourier filtering technique.

Shown in Figure 11 are two HREELS spectra acquired using an electron beam with a primary energy of $E_p = 42$ eV. Spectrum a of a clean Al$_2$O$_3$ film ($d_{AlO_2} = 8$ Å) exhibits two loss features at 615 and 885 cm$^{-1}$, assigned to the optical phonon modes of the Al$_2$O$_3$ film, and a nearly featureless base line at frequencies above 1000 cm$^{-1}$. The $^{15}$N$_2$ yield then reaches a maximum at $\theta_{Cu} \approx 1.3$ ($\sim$80 Å particles).

The adsorption of $^{15}$NO at 80 K on well-characterized particulate Cu deposits has been further studied using HREELS. The use of HREELS to address the nature of adsorbed species on oxide surfaces, however, suffers a significant handicap in that the accompanying vibrational spectra are dominated by losses due to excitation of surface optical phonons. The intense multiple phonon losses extend over a wide vibrational frequency range of the HREELS spectra, as is illustrated in Figure 2.
these loss features, the following paragraph summarizes the previous vibrational data of NO adsorbed on low index planes of single-crystal Cu.

There have been a few studies of NO adsorbed on low index planes of single-crystal Cu.34-38 These studies have shown that NO adsorption is quite complicated and that its decomposition chemistry is dependent on the surface orientation, the substrate temperature, and the exposure.34-38 HREELS studies,37 for example, have shown that, on Cu(110), NO initially adsorbs associatively at low temperatures (T < 110 K) in a skewed adsorption geometry (with the nitrogen end down). The loss features observed at ~840 and ~1560 cm^{-1} have been attributed to the NO bend, δ(NO), and the NO stretch, ν(NO), respectively, of a bent NO.37 In contrast, decomposition of a portion of the initially adsorbed NO occurs on Cu(100) even at T = 85 K, leading to the formation of adsorbed oxygen and nitrogen.37 The latter then combines with arriving NO molecules to form N2O at low exposures. The corresponding loss peaks observed at ~800 and ~1260 cm^{-1} are evident in the HREELS spectra and can be assigned to the NO bend and stretch, respectively, of a N2O species. The NN stretch of adsorbed N2O should give rise to a peak at ~2224 cm^{-1}, which was not detectable in the spectra.37 With an increase in NO exposure, first the loss features at ~770 and ~1500 cm^{-1} were observed followed by the loss peak at 1770 cm^{-1}. The 770 and 1500 cm^{-1} features were attributed to the δ(NO) mode and the ν(NO) mode, respectively, of skewed NO, and the 1770 cm^{-1} feature was ascribed to the ν(NO) mode of linear-bonded NO.37 On Cu(111), NO adsorption was associative at T = 85 K.36 Loss features at ~815 and ~1510 cm^{-1} were attributed to the vibrational modes of NO adsorbed on a bridging site of Cu(111).36 With an increase in NO exposure, first bridging and then atop NO species (at ~670 and ~1775 cm^{-1}) were found, and both were believed to be in a skewed adsorption geometry.36 Recent theoretical studies38 suggest that bridging NO with a bent bonding configuration on Cu(111) should exhibit a red shift in frequency by 713 cm^{-1} compared with the gas phase value of 1876 cm^{-1}. The bridging NO species was therefore reassigned to a 3-fold bonded NO.38

Considering the above discussion, we assign the loss feature at 1520 cm^{-1} to the NO stretch of 15NO species and the shoulder at ~1200 cm^{-1} to the NO stretch of a 15N2O species. The bending modes of 15NO and 15N2O were not observed in the present study because of the interference from the substrate phonon losses. The NN stretch of 15N2O also was not apparent due to the small perpendicular component of the dipole moment; i.e., the NN bond of adsorbed 15N2O probably lies parallel to the surface.

Reactions of Nitric Oxide and Carbon Monoxide with Particulate Cu. The reaction of nitric oxide and carbon monoxide with particulate Cu deposits supported on Al2O3 films has been studied using TPD and HREELS. 15NO and CO reactants were fully mixed in the gas manifold with a 15NO:CO ratio of 1:1 prior to admission into the UHV chamber. The adsorption of the gas mixture was then carried out via a gas doser at T = 80 K. Thermal desorption products from 15NO + CO adsorbed on the Cu particles have been followed by monitoring several masses (m/e = 28, 30, 31, 32, 44, and 46). Shown in Figure 12 are desorption signals for m/e = 28, 30, 31, 32, 44, and 46 following two different exposures. θCu in Figure 12 was 2.7, corresponding to a cluster size of ~105 Å. No desorption signal for m/e = 32 was observed in the 80–850 K temperature range, indicating the absence of gaseous O2 product. The desorption of the parent molecules of 15NO and CO and the gaseous products 15N2 and 15N2O, due to 15NO decomposi-
surface to the $^{15}$NO/CO gas mixture gives rise to several adsorbate loss features in the 1000–2500 cm$^{-1}$ frequency range. Very similar to $^{15}$NO adsorption, the 1255 and 1465 cm$^{-1}$ losses are attributed to the $\nu^{(15)}$NO mode of adsorbed $^{15}$NO and $^{15}$N$_2$O, respectively. The loss peak at 2110 cm$^{-1}$ is due to excitation of the carbon–oxygen stretch, $\nu$(CO), of adsorbed CO.

From the studies described above, the $^{15}$NO and CO reaction on particulate Cu can be summarized as follows:

$$^{15}\text{NO}_2(a) \rightarrow ^{15}\text{NO}$$
$$^{15}\text{NO}(a) \rightarrow ^{15}\text{N}(a) + ^{15}\text{O}(a)$$
$$^{15}\text{NO}(a) + ^{15}\text{N}(a) \rightarrow ^{15}\text{N}_2\text{O}$$
$$^{15}\text{N}(a) + ^{15}\text{N}(a) \rightarrow ^{15}\text{N}_2$$
$$\text{CO}(a) \rightarrow \text{CO}$$
$$\text{CO}(a) + ^{15}\text{O}(a) \rightarrow ^{15}\text{CO}_2$$

where the subscript (a) denotes an adsorbed species.

Conclusions

The reaction of nitric oxide and carbon monoxide on model Cu/Al$_2$O$_3$ catalysts has been studied using surface science techniques. The results can be summarized as follows:

1. Highly ordered, stoichiometric Al$_2$O$_3$ films can be successfully synthesized on a Mo(110) surface. The films (~20 Å thick) exhibit excellent thermal stability and chemical inertness toward adsorption.

2. The growth of particulate Cu deposits, prepared by vacuum vapor deposition, on the Al$_2$O$_3$ films has been studied in the 80–800 K substrate temperature range. The elevated substrate temperatures employed during Cu deposition significantly improved the crystalline quality and the thermal stability of the Cu deposits. A model based on Auger measurements has been utilized to examine the number density and the average size of the Cu particles. The number density of the Cu particles is estimated to be $1.4 \times 10^{11}$ cm$^{-2}$ at a substrate temperature of 600 K.

3. Nitric oxide decomposition on the Al$_2$O$_3$ supported Cu particles has also been investigated. TPD and HREELS data clearly show that a fraction of the $^{15}$NO molecules react with the Cu particles to produce gaseous $^{15}$N$_2$ and $^{15}$N$_2$O in the 90–250 K temperature range. The formation of $^{15}$N$_2$ at 770 K is also evident and is due to recombination of adsorbed $^{15}$N atoms from $^{15}$NO dissociation. The effects of retained oxygen, the adsorption temperature, and the particle size on the production of high-temperature $^{15}$N$_2$ were also examined.

4. The nitric oxide and carbon monoxide reaction has also been studied. The results showed that, besides the $^{15}$N$_2$ and $^{15}$N$_2$O products arising from NO decomposition, a small quantity of CO$_2$ was produced via the reaction between adsorbed CO and adsorbed oxygen.

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Appendix

As an approximation, the growth of three-dimensional particles in the Volmer–Weber (VW) mode can be simply described by two parameters: \( \theta \), the portion of the surface covered by the particles, and \( h \), the mean height of the particles. Conservation of mass leads immediately to

$$\theta h = d$$

where \( d \) is the thickness of equivalent monolayers.

In the VW mode, the Auger intensity associated with a particular transition of a substrate, \( I_s \), is given by

$$I_s = I_0(1 - \theta + \theta e^{-h/\lambda_s})$$

where \( I_0 \) is the peak intensity of the bare substrate and \( \lambda_s \) the attenuation length of the ejected Auger electrons of the substrate traveling through the adlayers. Likewise, the Auger intensity of the adlayers, \( I_a \), can be written as follows:

$$I_a = I_s e^{-h/\lambda_a}$$

Substituting \( d/\theta \) for \( h \) in eq 1, the ratio of \( I_a \) to \( I_s \) yields the following equation:

$$\frac{I_a}{I_s} = \frac{I_0}{I_s} \left(1 - \theta + \theta e^{-h/\lambda_s}\right)$$

Assuming that each particle grows in a hemispherical shape and that its morphology remains constant during growth, the dependence of \( \theta \) on \( d \) can be derived. The volume of a particle, \( V_s \), is equal to \( V = \frac{4}{3}\pi r^3 = h^2s \), where \( r \) is radius and \( s \) is the bottom area of the particle which is equal to \( \pi r^2 \). \( \theta \) can therefore be written in terms of the number of the particles, \( N_s \), and \( s \): \( \theta = N_s = 9\pi Nh^2/4 \). The dependence of \( \theta \) on \( d \), using eq 1 to eliminate \( h \), yields

$$\theta = (\frac{9\pi N}{4})^{1/3} d^{2/3}$$

The particular power in the above power law dependence does not require the assumption of the growth of hemispherical-shaped particles. It is a direct consequence of our simple growth model, and the power $2/3$ is a fingerprint for the quasi-isotropic growth. The detailed discussion of the quasi-isotropic growth model in terms of thermodynamic considerations has been given by Zhu et al.

The average particle size, \( 2r \), is easily obtained from the above derivation:

$$2r = \left(\frac{12\pi N}{4}\right)^{1/3} d^{2/3}$$

In the case of Cu/Al$_2$O$_3$, the attenuation lengths, \( \lambda_s \) (Cu-(LMM)) and \( \lambda_s \) (O(KLL)), are taken from the literature to be 15.040 and 10.1 Å, respectively. The value of $I_0/I_s$ is obtained from the standard Auger spectra of Cu and Al$_2$O$_3$. The density of Cu particles, \( N_s \), can then be computed using a curve-fitting procedure.

References and Notes

(2) Poppa, H. Vacuum 1984, 34, 1081.
(4) Iwamoto, M. In Future Opportunities in Catalytic and Separation Technology; Misono, M., Moro-oka, Y., Kimura, S., Eds.; Elsevier: Amsterdam, 1990; Vol. 54, pp 121–143.
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