Ultrahigh vacuum ESR studies on clean metal surfaces: NO$_2$ on copper a)

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While ESR has been applied extensively to study surface adsorbates and catalysis, almost no ESR is on clean surfaces prepared under UHV conditions. We report in this Communication our preliminary results using a new technique for the in situ study of molecular adsorption and reactions of gases on metallic surfaces prepared under UHV conditions. Our objectives are to comparatively study both "clean" and "real" metallic and related surfaces. Such studies should relate to the role of surface impurities and defects on the reactivity of metals. They have the added value that studies on real systems can signify those appropriate for more extensive UHV work. In particular, we report on NO$_2$ adsorbed on various Cu surfaces.

The heart of our design is the UHV-ESR resonant microwave cavity (cylindrical TE011 mode) with high unloaded Q (20,000) atenna-coupled to the microwave bridge and an integral part of the UHV system such that vacuum evaporation of clean metal films onto its interior surface may be performed. This is accomplished with a tungsten heater element that can be moved through one of the cavity stacks using a bellows drive. We have evaporated Ag and Cu on the inner surface of the ESR cavity under UHV conditions (10$^{-9}$–10$^{-10}$ Torr). The ESR sensitivity of this cavity is $\approx (N_{ssb})^{-1} \times 10^{12}$ spins per G, which is close to theoretical for this cavity design and wall loading. Given an effective surface area of the cavity of 50 cm$^2$ with perfectly smooth surfaces, or 10–100 times that for thin films produced by vacuum evaporation (which are typically very porous unless annealed), this yields a total of $\approx 10^{18}$–$10^{19}$ metal atom surface sites, comparing very favorably with $N_{ssb}$.

We summarize our results in order of increasing "cleanliness."

1. NO$_2$–Cu/Vycor system: The Cu metal supported on Vycor was prepared in the manner of Clarkson. The formation of Cu metal was confirmed by the red-pink color of the sample and no ESR signal due to Cu$^{2+}$. After exposing the sample with 0.1–1 Torr NO$_2$ at room temperature the sample color immediately changed to blue-gray, and a well-resolved ESR spectrum was obtained implying that the Cu on Vycor can be oxidized by NO$_2$ to form Cu$^{3+}$. The ESR spectrum (Fig. 1A) shows two types of Cu$^{3+}$ complexes with hyperfine and g-tensors for which we have a complete analysis. We tentatively

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FIG. 1. (A) ESR spectrum from NO$_2$/Cu/Vycor system showing well-resolved hfs; (B) ESR spectra from NO$_2$/Cu wire (+) of types a, b, and c (cf. text) and from UHV prepared Cu films + NO$_2$ (--.--). x-axis gives g-values; * shows NO$_2$ lines.
assign them to a distorted octahedral structure (formed from initially unreduced Cu²⁺) and to a distorted square planar structure (formed from Cu⁰). ¹ The well resolved Cu hfs indicates that these complexes consist of well-isolated Cu²⁺ ions on the Vycor surface.

(2) Cu wire: 99.999% pure Cu wire was precleaned by successive baking in H₂, O₂, then H₂. Small (several mg) samples could be introduced into the standard cavity in sample holders under vacuum (~10⁻⁶ Torr) without seriously affecting cavity Q. Properly cleaned samples show no ESR signals from Cu⁰. When NO₂ is admitted at 77 K ESR spectra of gas-phase molecular oxygen can be observed possibly from NO₂ decomposition. The reaction with Cu starts when NO₂ condenses at ~30°C and 5 Torr yielding species (a). Three types of ESR spectra (Fig. 1B) are observed: (a) symmetric singlet (gₑ = 2.19, ΔHₚₚ = 100 G); (b) asymmetric signal (gₑ = 2.41, gᵥ = 2.09); (c) asymmetric signal (gₑ = 2.34, gᵥ = 2.11). No hfs can be resolved. Normally an irreversible process occurs easily from species (a) to (c), and isolation of (b) requires the process to be frozen at lower temperature immediately after the formation of (a). Species (c), the final product of oxidation, could be the same as (or similar to) the first species seen on Cu/Vycor. The important spectral difference that hfs is seen for Cu/Vycor but not on Cu metal is attributed to the fact that, on the pure metal, adjacent sites become paramagnetic, so they can exchange-narrow the hfs, while on Cu/Vycor one only sees spectra from separated Cu²⁺ ions with negligible exchange interactions. The fact that the anisotropy in g-tensor is not averaged out on the pure metal is taken to imply that the Cu²⁺ ions are microscopically crystalline. ⁵ (Cu wire experiments have also been performed in the UHV system.)

(3) Experiments have been performed on evaporated Cu films on the inner surface of the UHV cavity with vacua of 10⁻⁹–10⁻¹₀ Torr after bakeout. Vacuum deposition of 99.999% Cu wire onto a Cu base for 10 min resulted in a mean thickness of film of 100–200 Å. Best experimental results are obtained by introducing NO₂ into the UHV system close to the ESR cavity rather than downstream nearer the UHV pumps, ion gauge, and mass analyzer. There is no evidence of O₂ formation with introduction of NO₂. (Our UHV-ESR cavity is particularly sensitive to the presence of paramagnetic gases which can fill the whole cavity.) A very high dosage of NO₂ (viz. flowing NO₂ at 10 mTorr for 1 min at ~100°C) is required before the reaction can be induced to occur, yielding a broad nearly symmetric ESR signal of over 100 G which is very similar to Spectrum a (Fig. 1), but no Spectrum c is found. Current experiments with O₂ and/or H₂O predosing and O₂/NO₂ mixtures indicate, consistent with the above, that O₂ and/or H₂O may play an effective role in causing Spectrum c to form.

These results indicate differences in properties of Cu/Vycor, Cu metal, and clean Cu films as well as differences between conventional and UHV preparations. Our UHV-ESR technique should be applicable to other metal films and to the preparation and study of "clean" oxide surfaces as well as "supported metal" surfaces.

Another intriguing feature of the UHV experiments is the observation of an intense g = 2 and narrow (ΔH ≈ 10 G) electron-cyclotron resonance at pressures less than 10⁻⁵ Torr. We propose that stray electrons can absorb enough microwave energy to knock additional electrons off the cavity walls to start an electron avalanche. This cyclotron resonance is quenched by the residual gas above 10⁻⁵ Torr and by microwave powers below a threshold value (Pₑ ~ 1–10 mW incident) needed to sustain a steady-state emission. We can use Pₑ to indicate how clean and free from defects is the Cu film. Fresh Cu films exhibit the highest Pₑ ~ 10 mW, while films heavily dosed with NO₂ exhibit very low Pₑ ~ 1 mW. Also Pₑ can be increased by biasing the electrically isolated endplate of the cavity.

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