ESR STUDIES OF SURFACE ADSORPTION AND CATALYSIS
UNDER ULTRA-HIGH VACUUM CONDITIONS

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ESR STUDIES OF SURFACE ADSORPTION AND CATALYSIS
UNDER ULTRA-HIGH VACUUM CONDITIONS

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ABSTRACT

This project is directed to developing ESR for the study of surface adsorption and catalysis on clean well-characterized metallic and oxide surfaces under UHV conditions and to compare the results of such studies with "real" surfaces, which are important in actual catalysis.

In this first year (since March) we have completed construction of the ESR-UHV system, and we have undertaken preliminary experiments with it, that have demonstrated the feasibility of the technique. With our newer ESR-UHV cavity we have achieved a sensitivity of 10^{12} spins per Gauss linewidth or close to theoretical.

We have also developed in situ techniques for ESR studies of surface adsorption and reactions of gases on 1) metals and oxides supported on crushed Vycor (ca. 1 torr); 2) metal wire and turnings and their oxides (ca. 1 torr); 3) metal powders (ca. 10^{-7} - 10^{-8} torr).

We observe, with NO_2/Vycor , temperature-dependent adsorbed NO_2 spectra which are amenable to a slow-tumbling analysis. A comparison of ^{63}Cu hyperfine parameters from NO_2 on Cu/Vycor vs. pure Cu has lead to the tentative conclusion that on the pure metal adjacent sites become paramagnetic, but the Cu^{2+} is forming on surfaces that are microscopically crystalline, so that adjacent Cu^{2+} ions have identical orientations of their g-tensor, although the macroscopic sample is poly-crystalline.

Related studies on the UHV-ESR cavity have been performed on the NO_2 -Cu/Vycor system.

An intense cyclotron resonance signal is observed in our UHV-ESR cavity at pressures less than 10^{-2} torr. It has a g-factor of 2.000, and it is attributed to microwave stimulation of exo-electron emissions (CREMSEE). It may also be suppressed by the use of reduced microwave power.

We have completed preliminary studies of oxygen ion radical (O_2^- and O^-) formation on partially reduced Ti on Vycor support. The process is greatly assisted by UV irradiation. Different types of O_2^- and O^- ESR signals are obtained and are correlated with differences in preparation and previous work with other supports.

ESR STUDIES OF SURFACE ADSORPTION
AND CATALYSIS UNDER ULTRA-HIGH VACUUM
CONDITIONS

Progress: (March - November 1)

A) Development and Evaluation of ESR-UHV Techniques

The initial phase of our work has been to develop the ESR-UHV technique. This involves the development of a UHV system that mates with the ESR spectrometer to permit high sensitivity studies under vacuum conditions to about 10^{-10} torr. The heart of the design is in the UHV-ESR resonant microwave cavity which must simultaneously 1) have excellent microwave properties (e.g. high Q, good microwave coupling to the spectrometer, and well-defined microwave modal pattern); 2) be an integral part of the UHV system; 3) allow for the vacuum evaporation of clean metal films onto the interior surface of the microwave cavity; 4) conform to the geometric constraints that permit its insertion into the magnetic-field gap; 5) permit temperature variation and control of the surface; 6) pass magnetic field modulation without excessive high frequency noise.

We have constructed the basic UHV-ESR system. This includes several designs of cylindrical microwave cavities that resonate in the TE₀₁₁ mode that is antenna-coupled via a UHV-UHF feedthrough to the microwave bridge, and that is an integral part of the UHV system. It also includes a feed-through with a tungsten heater element, which can be moved through one of the cavity stacks into the cavity under high vacuum by using a bellows drive. We have used this tungsten element to evaporate Ag and Cu on the inner surface of the ESR cavity under UHV conditions.

With our newer cavity design we have a sensitivity of the order of 10^{12} spins/gauss width. This is near the theoretical limit we estimate. The particular improvements include the use of very thin (20 mil) stainless steel cavity walls which allow us to use frequencies as high as 25 kHz field modulation, with only about a 20% attenuation through the walls. [We find that for modulation amplitudes of a few gauss, very little noise is generated, though the noise due to losses in the cavity walls increases rapidly if the modulation is increased beyond this level.] We have developed several other cavity designs which are currently being constructed. These include a ceramic cavity which should reduce noise from modulation of the cavity walls to a minimum, since the ceramic is very transparent to RF and is very rigid.

We have now performed several experiments with the UHV-ESR system that are discussed below. We have been able to obtain initial pressures of the order of 10^{-9} torr. with our system, and we anticipate pressures as low as 10^{-10} torr as our techniques improve.

B) High Vacuum Experiments on Surface Catalysis

We have embarked on a series of experiments ranging from "real" surfaces, which are important in actual catalysis to surfaces which approximate the "clean" surfaces one achieves by UHV techniques. These experiments are designed to be done in conjunction with our UHV experiments. They are designed to serve as background for providing preliminary insight into the related but more difficult UHV experiments and also to enable us to study similarities and differences between the "clean" and well-characterized surfaces and the "real" surfaces. These studies include:

- 1) metals and oxides supported on crushed vycor with gases at ca. 1 torr;
- 2) metal wire and turnings and their oxides with gases at ca. 1 torr;
- 3) metal powders with

gases at ca. 10^{-7} - 10^{-8} torr; 4) UHV experiments 10^{-9} - 10^{-10} torr.

We have found that a particular system viz. NO_2 on copper is an especially useful one for our initial efforts which are focussed on developing our methods. We summarize our various types of results on this system.

1) NO_2 -Cu/Vycor System

The Vycor was prepared and activated in the same manner as Clarkson. It was immersed in 0.05-0.1 M aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. The mixture is allowed to stand for 24 hours at RT, then filtered and dried overnight. The sample is then evacuated at ca. 10^{-6} torr, and then reduced under 1 atm of H_2 at 500°C to produce supported Cu metal. The formation of Cu metal was confirmed by the red-pink color of the sample and no ESR signal due to Cu^{2+} ; (the color of Cu^+ should be brown or white). After exposing the sample to NO_2 with 0.1 - 1 torr pressure at room temperature, the sample color immediately changed to blue-gray and a well-resolved ESR spectrum of ^{63}Cu was observed, implying that the Cu on Vycor can be oxidized by NO_2 to form Cu^{2+} (e.g. $\text{Cu}^0 + 2\text{NO}_2 \rightarrow \text{Cu}^{2+} + 2\text{NO}_2^-$). The ESR spectrum (cf. Fig. 1) shows two types (II and III) of Cu^{2+} complexes, and the hyperfine and g-tensors appear in Table I. Based upon single crystal ESR studies of copper complexes by other workers (cf. Table Ib) we tentatively assign them to a distorted octahedral structure (type II, formed from initially unreduced Cu^{2+} , see below) and to a distorted square planar structure (type III, formed from Cu^0). If the Cu^{2+} /Vycor is only partially reduced in H_2 (e.g. at 150°C) (or else unreduced) another type (I) of Cu^{2+} complex is observed (cf. Fig. 2). On the other hand, baking ($\geq 400^\circ\text{C}$) leads to this type I spectrum being supplanted by a single broad line (type IV). This sequence is interpreted as follows. The Cu^{2+} ions in the initial state have a distorted square planar configuration

in which Cu^{2+} ions are co-ordinated by H_2O (or OH^-) and NO_3^- ions (Type I). Admission of NO_2 gases leads to an exchange of the ligands from H_2O (or OH^-) to NO_2^- (e.g. by reaction $\text{NO}_2 + \text{OH}^- \rightarrow \text{NO}_2^- + \text{OH}$), and to a change in the configuration probably to a distorted octahedral as indicated by the ^{63}Cu ESR spectral parameter changes (Type II).

The well resolved ^{63}Cu hyperfine structure of types I, II, and III indicates that these complexes are formed from well-isolated Cu^{2+} atoms on the Vycor surface. However, the annealing leading to the type IV spectrum is probably causing clustering of Cu^{2+} into a single exchanged ESR line.

We also note that ESR spectra are obtained from NO_2 adsorbed on the pure and metal supported Vycor and is discussed further below. We also observe the species $^{14}\text{NO}_2^{2-}$ adsorbed on the Vycor. One possible reaction forming NO_2^{2-} may be: $\text{Cu}^{2+} + \text{NO}_3^- \rightarrow \text{Cu}^+ + \text{NO}_2^{2-} + (1/2)\text{O}_2$. We compare in Table II its magnetic parameters with NO_2^{2-} obtained in other systems.

2) NO_2 /Copper Metal

When NO_2 is admitted, the reaction starts at -30°C , just as in the Cu/Vycor system. Three types of EPR spectra are observed: (A) symmetric singlet ($g = 2.19$, $\Delta H_{\text{pp}} = 100$ G); (B) asymmetric signal ($g_{\parallel} = 2.41$, $g_{\perp} = 2.08$); (C) asymmetric signal ($g_{\parallel} = 2.34$, $g_{\perp} = 2.07$). No hyperfine splittings can be resolved (Fig. 3). Normally an irreversible process occurs easily from species (A) to (C), as shown by the sequence of spectral changes in Figure 3. Transition from species (A) to (B) can be observed only if the process is frozen at lower temperature immediately after the formation of species (A). Species (C) is the final product of this oxidation process of Cu metal and disappears after heating and degassing.

We note from Table 1 that species C could be the same species as II seen on the Cu/Vycor system. The important spectral difference that II shows hfs while C does not, 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 sees spectra from separated Cu^{2+} ions with negligible exchange interactions. The fact that the anisotropy in the g-tensor is not averaged out on the pure metal is taken to imply that the Cu^{2+} ions are on surfaces that are microscopically crystalline, so that adjacent Cu^{2+} ions have identical orientations with respect to the dc magnetic field. (Of course, the macroscopic sample is poly-crystalline.) These intriguing results indicate the rather different properties of Cu/Vycor and pure Cu metal, and also show the importance of performing such comparative experiments.

The role of species A is less clear. Perhaps it represents an initial cluster formation, due to localized oxidation of Cu, which then arranges itself in micro-crystalline form on the surface, thus yielding spectrum B (with the same g_{av}).

We also note that O_2 signals were detected in the sample tube at low temperatures ($< -80^\circ\text{C}$). This might be attributed to the equilibrium concentration of O_2 from the dissociation of NO_2 : $\text{NO}_2 \rightleftharpoons \text{NO} + 1/2\text{O}_2$. However, the presence of O_2 might be responsible for the catalytic process of the oxidation on Cu metal surfaces (see below).

CuO samples were prepared [by oxidizing the H_2 -reduced Cu turnings with 1 atm O_2 at different elevated temperatures]. Immediately after the NO_2 gas is leaked in at 77°K , ESR spectra of molecular oxygen can be observed. Otherwise similar spectra to those obtained when starting initially with the reduced Cu sample are seen. The main point is the greatly increased reactivity of the CuO vs. the pure Cu with NO_2 according to $\text{NO}_2 \rightarrow \text{NO} + 1/2\text{O}_2$. The pure Cu is first oxidized at ca. -30°C by

e.g. $\text{Cu} + \text{NO}_2 \rightarrow \text{CuO} + \text{NO}$ before it can catalyze the formation of oxygen.

3) UHV Experiments with Cu and NO_2

The more conventional ESR experiments discussed have shown that copper metal reacts with NO_2 to form Cu^{+2} complexes. Preliminary experiments have been performed with the UHV system with freshly deposited copper and gaseous/liquid NO_2 . Leaking in NO_2 at 10^{-7} to 10^{-6} torr at room temperature results in the dissociation of NO_2 as observed on the mass analyzer. When the cavity is heated afterwards to ca. 70°C NO is rapidly outgassed as observed on the mass analyzer. We do not see an ESR signal from adsorbed NO. Ito, Abe, and Suetaka [J. Cat. 57, 80 (1979)] have found that NO chemisorbed on nickel and palladium exists mainly as a cis-dimer for high coverages at room temperature. This dimer would not be observed by ESR if it were diamagnetic. The oxygen is seen on the mass analyzer while NO_2 is leaked in or when the cavity is heated afterwards. The oxygen may be reacting with carbon and/or carbon compounds on the walls in the vacuum system to form CO and CO_2 . If NO_2 is leaked in over long periods ($\frac{1}{2}$ hour) a peak due to NO_2 is eventually observed on the mass analyzer.

In another experiment the cavity was cooled to -40 to -50°C in the presence of 2 torr NO_2 and this results in bulk condensation of NO_2 as observed by a large pressure drop. Gas phase ESR signals from both NO and NO_2 are observed but not O_2 . No reaction occurs so as to produce observable Cu^{+2} (paramagnetic) species. As a result of pumping to 10^{-7} torr and heating the walls of the cavity, there is a marked increase in peaks on the mass analyzer due to NO, N_2O , and NO_2 .

It is postulated that either the presence of O_2 is needed to oxidize Cu by NO_2 or the presence of NO poisons this reaction. Experiments are planned in which a) O_2 is

chemisorbed before NO_2 is leaked in, or b) a mixture of NO_2 and O_2 is used or c) an oxide layer is formed by heating the deposited copper with O_2 .

A background signal is however observed. It becomes very weak when the system is brought in contact with air, but it increases as the system is pumped and baked out. It consists of a broad signal with a peak to peak linewidth of 175G with a sharper, but inverted (out of phase) signal with a linewidth of 10G. Signals similar to this are observed for Ni^{+2} in MgO . [Cf. Wertz et al, Phys. Rev , (1969)].

C) Oxygen ion radicals formed on Ti/Vycor

Oxygen ion radicals, O_2^- and O^- , are formed by an electron transfer reaction from Ti^{3+} on Ti/Vycor to O_2 and O . This reaction may be assisted by U.V. light.

1) Sample: The Ti-containing samples were prepared by impregnation of porous Vycor glass by aqueous TiCl_4 solution. The samples were dried at 80°C and then calcinated in air for several hours at 500°C . Before studying the adsorption of O_2 or N_2O gases, the samples were placed into a 3mm o.d. spectroil ESR tube evacuated, heated in 1 atm. O_2 , reduced with 1 atm. H_2 and finally evacuated to 10^{-6} torr at 500°C .

2) O_2^- formed by O_2 adsorption on partially reduced Ti supported on Vycor (no U.V. light).

Two different types of O_2^- were observed after admission of O_2 gases to the sample at RT; $\text{O}_2^-(\text{I})$: $g_1 = 2.0305$, $g_2 = 2.008$, $g_3 = 2.0140$; $\text{O}_2^-(\text{II})$: $g_1 = 2.023$; $g_2 = 2.0094$, $g_3 = 2.0035$ at 77K. Both signal intensities increased with O_2 gas pressure up to 5 torr. The $\text{O}_2^-(\text{I})$ is the predominant species in the case of admission of O_2 at RT, but $\text{O}_2^-(\text{II})$ could be separately observed from $\text{O}_2^-(\text{I})$ when the sample was heated with 1 atm O_2 at 400°C and then evacuated at the same temperature.

Although Shvets and Kazansky [Phys. Rev. 178, 471(1969)] have reported two types

of O_2^- ($g_1^I = 2.026$, $g_1^{II} = 2.020$, $g_2 = 2.009$, $g_3 = 2.003$ at 77K) formed on Ti/SiO_2 , the g-values of the present $O_2^-(I)$ and $O_2^-(II)$ are fairly different from those reported by them. The g-values of $O_2^-(I)$ and $O_2^-(II)$ are very close to O_2^- formed on TiO_2 (rutile) and TiO_2 (anatase)-(Naccache et al, J.C.S. Faraday Trans. III 67, 506, 1971), respectively. (Further data may be found in Table III.)

3) O_1^- , O_2^- formed by U.V. irradiation of $Ti/Vycor$ with O_2

The $Ti/Vycor$ with 2 torr O_2 was irradiated at RT or 77K using a high pressure Hg lamp (main wave length 257 nm) without a filter. The new O_2^- ($O_2^-(III)$): $g_1 = 2.0260$, $g_2 = 2.0091$, $g_3 = 2.0033$ at 77K) appeared after several minutes irradiation at 77K together with a weak signal due to $O^-(I)$ having $g_1 = 2.0020$, which probably comes from decomposition of O_2^- or O_2 on the surface by U.V. light. Upon warming the sample to RT for several minutes, the $O^-(I)$ signal disappeared completely and the $O_2^-(III)$ signal intensity decreased slightly. At the same time, two new signals appeared at $g = 2.0455$ and $g = 2.0303$ (at 77K).

The signal at $g = 2.0455$ has never been reported before for the adsorption O_2 on Ti/SiO_2 or TiO_2 systems, but the value is very close to g_1 of O^- on MgO (Nacchache, Chem. Phys. Letters, 11, 323, 1971). Therefore, it is reasonable attribute this species to $O^-(II)$ stabilized at a preferred site, $O^-(I)$ serving probably as a precursor of $O^-(II)$. The $O^-(II)$ species was stable at RT, but the spectrum could not be observed clearly at RT because of line broadening.

The signal at $g = 2.0303$ is easily attributed to g_1 of $O_2^-(I)$ mentioned above. It was concluded from the temperature dependence of the spectrum that the mobility of $O_2^-(IV)$ on the surface was much higher than that of $O_2^-(I)$ and the thermal stability of $O_2^-(III)$ was less than that of $O_2^-(I)$. These findings indicate that some of the $O_2^-(III)$

formed by U.V. irradiation at 77K might move to a more stable site to form $O_2^-(I)$ upon warming.

The U.V. irradiated Ti/Vycor with O_2 at RT gave the $O_2^-(I)$, $O_2^-(III)$ and $O^-(II)$, but not $O^-(I)$. The $O_2^-(III)$ decays and only the signals of $O_2^-(I)$ and $O^-(II)$ are observed after keeping the sample at RT for 1 week.

4) O^- , O_2^- formation by decomposition of N_2O on Ti/Vycor surface using U.V. light.

No signal was observed after admission of N_2O to the partially reduced Ti/Vycor sample at RT. When the sample containing 2 torr N_2O was irradiated at 77K for several minutes, the strong signal due to O_2^- , type III ($O_2^-(III)$), appeared together with a weak signal having a partially resolved structure at $g = 2.0027$ region; this latter signal is not yet identified.

Upon warming the sample to RT, the unidentified signal decayed, and was replaced by a signal at $g = 2.0455$, which is attributable to $O^-(II)$. Interestingly, in this system, the $O_2^-(III)$ species was more stable than that for the O_2 /Ti/Vycor system and the g-values were slightly changed after keeping the sample at RT for 24 hours. Furthermore, no signal from $O_2^-(I)$ was observed.

Thus, the phenomenon of stabilization of O^- or O_2^- is quite different for the two systems of O_2 /Ti/Vycor and N_2O /Ti/Vycor, and we are carrying out further studies on these systems.

D) Cyclotron Resonance from Microwave Stimulated Exoelectron Emissions

(CREMSEE)

Electron cyclotron resonance is observed in our UHV cavities at pressures less than 10^{-2} torr. The signal was found to be independent of pressure below 10^{-4} torr; above 10^{-4} torr it becomes noisy and erratic. The signal is intense, because electric dipole transitions are usually 10^4 times as strong as magnetic dipole transitions. Also, it shows an extremely non-linear power dependence.

The signal consists of two "windows" cut out of an absorption which has a peak intensity at $g = 2.0000 \pm .0008$ (for cyclotron resonance $h\nu/\beta H = g = 2$). It has neither a Gaussian nor a Lorentzian lineshape. The edges of these windows correspond to discontinuities in the absorption signal, (cf. Fig. 4). Thus, it is found that changing the magnetic field or power level by a fraction of a Gauss or dB, respectively, will induce a signal that can saturate the detection system. A plot of these critical field/power values are shown in Fig. 5. As power is increased, these two windows will eventually merge.

Very sharp features (or "noise") are also observed on top of the cyclotron resonance signal. These features are reproducible only on a short time ($\sim$ minutes) basis and appear to be due to instabilities resulting from microphonics. Varying the pressure between 10^{-9} to 10^{-3} torr. by either leaking in N_2 and/or by throttling the UHV pumps results in no change in either the intensity or the critical power field values for the signal. Since the mean free path for N_2 is greater than the cavity dimensions below 10^{-2} torr, it is proposed that strong electrons can absorb successive microwave quanta without loss in phase memory, and, if no collision occurs with residual gas molecules, the electron can gain enough energy (rotational) to knock an electron off the

wall, thus starting an electron avalanche. Indeed, if a teflon sheet is placed next to the cylindrical walls of the cavity, where no cyclotron resonances absorption occurs since this is a region of low electric RF field, a complete quenching of CREMSEE is observed at all powers.

Our cavities operate in the TE₀₁₁ mode, for which the RF electric field is a maximum and perpendicular to the DC magnetic field in two regions. However, the RF field in each region is 180° out of phase with the other. Thus if an electron absorbs energy in one region, when it drifts into the other it will emit energy. Thus, it is proposed that the presence of a second window shifted away from $g = 2.000$ is due to this phase difference. The shift of 5 gauss corresponds to the cyclotron resonance frequency being $\pi/500$ radians per period out of phase with the RF field. If the transit time between the regions of strong RF field were 5×10^{-8} an electron could start out in synchronization with the RF and still be in synchronization while it was in the other region. This transit time corresponds to 4×10^6 cm/sec as compared to an average velocity of a thermal electron, 1.1×10^7 cm/sec. To test this hypothesis a teflon sheet was placed across the cavity in the region where the component of the electric RF field perpendicular to the DC field is zero in order to separate the two regions where the perpendicular component is a maximum. This results in only one window in the spectrum due to discontinuities only in the first derivative, not the absorption curve. As the power is decreased to ~ 1 mW, the size of the window reduces to only 7 gauss. The signal quickly becomes weak, erratic, and noisy as the power is further reduced. Thus there is no longer a critical power at which the CREMSEE started.

A somewhat similar effect to CREMSEE has been observed by Watt, Hand and Schneider [J. Phys. A, L25, 1971, 4(2)], but those workers had to use an external voltage

to initiate and sustain the cyclotron resonance signal at powers of 1mW. In addition those workers observed a marked pressure dependence of the critical power required to initiate the electron avalanche. While we have recently observed some pressure dependence when CO or CO₂ is leaked in the system, no change in critical power or field values was observed. We are ready to perform experiments using a DC electric field to 1) see if the CREMSEE can be altered to that it does not interfere with ordinary ESR signals, 2) to help in further understanding this effect.

We have implicated the metal surface as a source of the electron avalanche. In a recent experiment, a four-fold increase in the minimum critical power to initiate CREMSEE was observed after sublimation of a fresh copper film on the cavity walls. Exposing the cavity to ~ 10 torr NO₂ and pumping out the system resulted in the complete reversal of this change. In further experiments attention will be paid more closely to how the CREMSEE is affected by surface treatment, with the possibility that CREMSEE could be correlated to the condition of the surface.

E) Studies of Motional Dynamics of Radicals on Surfaces

We have observed ESR and ST-ESR spectra of NO₂ adsorbed on the pure Vycor, metal ions (such as Cu²⁺, Ti⁴⁺) supported on Vycor, and Zeolite (containing Al⁻ and Na⁺) over the temperature range from 4K to the temperature of NO₂ desorption. These spectra are temperature-dependent; i.e. one sees frozen-state spectra at 4K, but there is gradual averaging as the rotational motion increases when the temperature is raised. Our preliminary experiments show that the nature of the NO₂ molecular motion is quite different on those three different surfaces, probably strongly affected by the electrostatic field due to the metal ions.

These slow-tumbling spectra should be amenable to analysis by means of our

slow-motional theory thus permitting the study of motional dynamics on surfaces.

The O_2^- radical ions stabilized on Ti^{4+} supported Vycor surfaces are also found to exhibit temperature-dependent spectra which are amenable to analysis by our slow motional theory.

Table 1a ESR parameters of Cu(II) ion complexes (present works)

Type of Cu(II) complexes	Hyperfine G (cm^{-1})		g-value		Temp.	System
	$A_{ }$	$A_{\perp}$	$g_{ }$	$g_{\perp}$		
Type I	157.7 (168.8×10^{-4})	$< \Delta H$ (line width)	2.292	2.052	-196°C RT	$\text{Cu}^{2+}/\text{Vycor}$
I'	145 (156×10^{-4})	$< \Delta H$	2.301	2.039	-120°C	$\text{NO}_2/\text{Cu}^{2+}/\text{Vycor}$
Type II	133.9 ± 1.3 ($147.8 (\pm 1.4) \times 10^{-4}$)	$< \Delta H$	2.3634	2.052	-196°C RT	$\text{NO}_2/\text{Cu}^{2+}/\text{Vycor}$
II'	127.5 (140.6×10^{-4})	$< \Delta H$	2.361_3	2.0384	-120	$\text{NO}_2/\text{Cu}^{2+}/\text{Vycor}$
II''	133.0 ± 2.5 ($145.6 (\pm 2.7) \times 10^{-4}$)	20.5 ± 2.5 ($19.6 (\pm 2.4) \times 10^{-4}$)	2.344_7	2.0490	RT -196	$\text{NO}_2/\text{Cu}^{2+}/\text{Vycor}$
Type III	177.5 ± 1.2 ($188.9 (\pm 1.3) \times 10^{-4}$)	24.9 (23.8×10^{-4})	2.279_4	2.0462	-196 RT	$\text{NO}_2/\text{Cu metal}/\text{Vycor}$
Type IV	$< \Delta H$	$< \Delta H$	$g_{\text{iso}} = 2.1596$ $\Delta H = 250 \text{ to } 420$ (65°C) (-140°C)			$\text{Cu}^{2+}/\text{Vycor}$

Table 1b ESR parameters of Cu(II) ion complexes (previous works)

Type of Cu(II) complexes	Ref.	System	ESR Parameters Hyperfine G (or cm^{-1})		g-value		Temp.	Note
			$A_{\parallel}$	$A_{\perp}$	$g_{\parallel}$	$g_{\perp}$		
CuCl_4^{2-}	(4)	single crystal Cs_2CuCl_4	$A_1 = (5.1 \pm 0.5) \times 10^{-3} \text{ cm}^{-1}$ $A_2 = (4.6 \pm 0.5) \times 10^{-3} \text{ cm}^{-1}$ $A_3 = (2.5 \pm 0.5) \times 10^{-3} \text{ cm}^{-1}$		$g_1 = 2.083 \pm 0.051$ $g_2 = 2.103 \pm 0.003$ $g_3 = 2.384 \pm 0.003$		77K	Tetrahedral
$\text{Cu}(\text{H}_2\text{O})_6^{2+}$ or 4	(1)	Zeolite	120G ($133 \times 10^{-4} \text{ cm}^{-1}$)	22G	2.37	2.07	77K	Octahedral (or tetrahedral)
$\text{Cu}(\text{NH}_4)_4^{2+}$	"	"	175G ($184 \times 10^{-4} \text{ cm}^{-1}$)	-	2.25	2.04	"	close to square planar (or tetragonal)
$\text{Cu}(\text{C}_5\text{H}_5\text{N})_4$	"	"	185G ($193 \times 10^{-4} \text{ cm}^{-1}$)	$A_{\perp} = 16 \text{ G}$	2.24	2.03	"	
$\text{Cu}(\text{H}_2\text{O})_4^{2+}$	(3)	silicate layer	$175 \times 10^{-4} \text{ cm}^{-1}$		2.33	2.08	77K	
$\text{Cu}(\text{H}_2\text{O})_6^{2+}$	"	"	$145 \times 10^{-4} \text{ cm}^{-1}$		2.38	2.16	"	Octahedral with tetragonal distortion
$\text{Cu}(\text{C}_5\text{H}_5\text{N})_4^{2+}$ (type A)	(2)	SiO_2	$170 \times 10^{-4} \text{ cm}^{-1}$		2.276	2.037	77K	distorted octahedral or tetragonal
$\text{Cu}(\text{C}_5\text{H}_5\text{N})_4^{2+}$ (type B)			$120 \times 10^{-4} \text{ cm}^{-1}$		2.327	2.051	77K	tetrahedral

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Table 2 ESR parameters of $^{14}\text{NO}_2^{2-}$

<u>System</u>	<u>Hyperfine and g-values</u>	<u>Temp(°C)</u>	<u>Ref.</u>
$\text{Cu}^{2+}/\text{Vycor}$	$A_{\text{max}} = 34.56; g_{\text{max}} = 2.0021$	+20	Present work
	$A_{\text{max}} = 37.02; g_{\text{max}} = 2.0020$	-196	"
KCl	$A_x = 30.9, A_y = 5.0, A_z = 7.0$ $[g_x = 2.0038, g_y = 2.0099, g_z = 2.0070]$		(1)
KNO_3	$A_x = 31.3, A_y = 3.5, A_z = 3.5$ $[g_x = 2.004, g_y = 2.010, g_z = 2.008]$		(2)
ZnO	$A_z = 38, g_z = 2.0026$	-196	(3)
MgO	$A_{ } = 33, A_{\perp} < 10; g_{ } = 1.996, g_{\perp} = 1.89$ $\pm 0.001 \quad \pm 0.01$	+23	(4)
TiO_2	A) $A_{ } = 31.9, A_{\perp} \approx 0; g_{ } = 2.0045, g_{\perp} = 2.0065$ B) $A_{ } = 31.3, A_{\perp} \approx 0; g_{ } = 2.0040, g_{\perp} = 2.0060$ C) $A_{ } = 31.3, A_{\perp} \approx 0; g_{ } = 2.0042, g_{\perp} = 2.0062$	RT	(5)

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Table 3 g-values of O_2^- , O^- species formed on Ti/Vycor system (present studies)

Species	Temp.	g-value				Note
		g_1	g_2	g_3	g_{av}	
O_2^- (I)	RT	2.0295	2.0093	2.0034	2.0141	O_2 - Ti/Vycor, adsorption at RT
	77K	2.0305	2.0088	2.0027	2.0140	
O_2^- (I')	RT	2.0297	2.0090	2.0030	2.0139	O_1 - Ti/Vycor, UV (257mm) without filter at RT or 77K (formed upon warming to RT).
	77K	2.0303	2.0090	2.0022	2.0138	
O_2^- (II)	RT	2.0223	2.0093	2.0037	2.0118	O_2 - Ti/Vycor, observed at 400°C Stable at RT
	77K	2.0237	2.0094	2.0035	2.0122	
O_2^- (III)	RT	2.0219	2.0087	2.0077	2.0128	O_2 - Ti/Vycor, UV at RT or 77K. Rather unstable at RT (slowly decaying).
	77K	2.0260	2.0091	2.0033	2.0128	
O_2^- (III')	RT	2.0218	2.0097	2.0073	2.0129	N_2O - Ti/Vycor, UV at 77K keeping the sample at RT for 20 hours - stable at RT
	77K	2.0256	2.0089	2.0042	2.0129	
O^- (I)	RT	unstable at RT				O_2 - Ti/Vycor UV at 77 probably $g_{ } > g_{\perp}$
	77K	$g_{ } = ?$		$g_{\perp} = 2.0020$		
O^- (II)	RT	undetectable because of line broadening				stable at RT O_2 or N_2O - Ti/Vycor UV at 77 formed upon warming to RT
	77K	$g_{ } = ?$		$g_{\perp} = 2.0455$	probably $g_{\perp} > g_{ }$	

Table 3' g-values of oxygen radical ions formed on Ti/SiO_2 , TiO_2 and other oxides
(previous studies)

Species	Ref.	System	Temp.	g-value				Notes
				g_1	g_2	g_3	g_{av}	
O_2^- (A)	(1)	$\text{O}_2/\text{Ti/SiO}_2$	77K	2.020 ± 0.001	2.009 ± 0.001	2.003 ± 0.001	2.011	
O_2^- (B)	"	"	"	2.026	2.009	2.003	2.013	$-\text{O}_2^-$ (III)
O^-	"	$\text{N}_2\text{O/Ti/SiO}_2$ (UV)	"	$g_{ } = 2.011, g_{\perp} = 2.002$			2.005	$-\text{O}^-$ (I)
O_2^- (A1)	(2)	O_2/TiO_2 (Anatase)	77K	2.025	2.009	2.003	2.012	$-\text{O}_2^-$ (III')
" (A2) ₁	"	"	"	2.024	2.009	2.003	2.012	$-\text{O}_2^-$ (II)
" (A2) ₂	"	"	"	2.020	"	"	2.011	
O_2^- (R) ₁	"	O_2/TiO_2 (Rutile)	"	2.030	2.008	2.004	2.014	$-\text{O}_2^-$ (I)
" (R) ₂	"	"	"	2.020	2.009	2.003	2.011	
O^-	(3)	$\text{N}_2\text{O/MgO}$ (UV)	"	$g_{ } = 2.041, g_{\perp} = 2.0016$				$-\text{O}^-$ (II)
O_2^-	(4)	$\text{O}_2/\text{W/SiO}_2$	77K 418K	2.0266 $g_{ } = 2.007, g_{\perp} = 2.018$	2.0097	2.0042	2.0135 2.014	close to O_2^- (III) or (III')
O_2^- (A')	(5)	O_2/TiO_2	RT	2.019	2.010	2.005	2.011	
(B')			"	2.023	"	"	2.013	
(C')			"	2.026	"	"	2.014	
O_2^-	(6)	$\text{O}_2/\text{Ag/Vycor}$	RT	2.034	2.0115	2.0042	2.0166	
O_2^-	(7)	O_2/TiO_2 (UV)	77K	2.021	2.009	2.001	2.010	
O_3^-		"	"	2.014	2.009	2.003	2.008	
O_3^{3-}		"	"	$g_{ } = 2.008, g_{\perp} = 2.001$			2.003	
$\text{O}_2^- \text{CO}^-$		" + CO	"	2.0465	2.006	2.001	2.0178	

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FIGURE 1. ESR spectrum obtained after exposing the copper metal supported on Vycor to 1 torr NO_2 at room temperature followed by cooling to 93°K . This spectrum corresponds to the type III Cu^{2+} complex together with a weak spectrum due to the type II Cu^{2+} complex (cf. Table 1).

FIGURE 2. ESR spectra of copper $\text{Cu}(\text{NO}_3)_2$ supported on Vycor after evacuating and treating with 1 atm. H at 150°C . A) and B) are spectra recorded at -120°C . before and after the admission of 3 torr NO_2 respectively. The spectrum C) was recorded at -120°C after first warming to room temperature and evacuating for 12 hours to remove excess NO_2 . An anisotropic triplet marked with * corresponds to NO_2 adsorbed on Vycor. Also g_{DPPH} corresponds to the g -value of DPPH ($g=2.0036$). The co-existence of the two types of Cu^{2+} formed: I and II is shown in spectrum B.

FIGURE 3. ESR spectra from reaction of NO₂ with clean copper metal at -30°C. The upper, middle, and lower spectra correspond to types A, B, and C Cu²⁺ ions respectively, (cf. Text).

FIGURE 4. EPR spectrum (first derivative of cyclotron resonance of free electrons in a TE011 mode UHV cavity (CREMSEE). Microwave power: 1.8 mW; modulation amplitude: 0.08 Gauss; modulation frequency: 270 Hz; gain x 1.25 ; room temperature; pressure: 10^{-7} torr.

FIGURE 5. Curve showing critical magnetic field-microwave power values required to initiate CREMSEE. Shaded region - domain for which CREMSEE is observed.