The Surface Structure and Associated Rehydration Phenomena Observed on Cu/Al$_2$O$_3$

Immediately after 0.5% Cu/Al$_2$O$_3$ is prepared it has spectral characteristics significantly different from this material after equilibration in the laboratory with ambient moisture. The diffuse reflectance spectrum of freshly prepared material is significantly more intense than the spectrum of the equilibrated sample. In addition the EPR spectrum of the freshly prepared material displays a significantly smaller $g_\parallel$ value yet a larger $A_\parallel$ value than the corresponding spectral parameters obtained for the equilibrated sample. A model is proposed in which the freshly prepared, dehydrated surface finds the Cu(II) ions in essentially sites of C_{4v} symmetry while the hydrated (equilibrated) surface finds the Cu(II) ion in sites of D_{4h} symmetry.

Several investigators (1–7), using a variety of techniques, have examined the disposition of copper supported on γ-Al$_2$O$_3$. The picture which has developed through these studies is one in which the Cu(II) ion, depending upon its concentration, is distributed to varying degrees either in clusters or in relative isolation on the surface. An early report (3) proposed open octahedral or C_{4v} site symmetry for the isolated, well-dispersed Cu(II) ions. Although bonding parameters were derived for this site from the reported EPR spectra and associated spin-Hamiltonian parameters, little convincing experimental evidence was presented to support the identity of this specific site.

In examining this system further at low Cu(II) concentration one feature which consistently stands out among a variety of experimental conditions and variables is the gradual transformation which takes place as the supported material is exposed to ambient moisture. This note will present evidence to support the proposed C_{4v} surface site as well as explain the observed transformation of the material as a function of aging.

EXPERIMENTAL

The alumina used in this investigation was RA-1 γ-Al$_2$O$_3$ obtained from Reynolds Metals Company. It has a reported surface area of 225 m^2/g and an iron impurity level of 0.5%. X-Ray powder diffraction patterns confirmed the exclusive presence of the γ-phase. The alumina was ground and sieved retaining only 20- to 30- mesh-size particles. These particles were subsequently impregnated with aqueous Cu(NO$_3$)$_2$. These samples, containing 0.5% Cu(II) (Al$_2$O$_3$ basis), were dried at 120°C and finally calcined at 600°C for 2 hr in oxygen or *in vacuo* (nominal 10^{-2} Torr).

Optical reflectance spectra were collected in the spectral range 2000 to 220 nm using a Beckman DK-1A spectrophotometer equipped with a reflectance attachment. All spectra were run against γ-Al$_2$O$_3$ prepared under conditions identical to those used to prepare the Cu/Al$_2$O$_3$ samples. The reflectance spectra were converted into absorption spectra using the individual particle scattering theory of Melamed (8). The conversion procedure has been shown to give absolute absorption values in excellent agreement with transmission experiments. A refractive index of 1.65 was used in the Melamed conversion procedure. This value was verified experimentally, with no detectable difference noted between freshly prepared material and material allowed to equilibrate with ambient moisture.

Electron paramagnetic resonance spectra were obtained with a Bruker ER-420 spectrometer at both room temperature and

boiling-liquid-nitrogen temperature. The X-band frequency was measured with the Bruker BX-FMD frequency counter while the field was determined with the Bruker B-NM12 NMR gaussmeter.

Samples prepared at 600°C in oxygen or in vacuum were transferred to the appropriate EPR sample tube and sealed under either of the above atmospheric conditions. The reflectance spectra of the samples were taken immediately after the samples cooled to room temperature in sealed reflectance cells. Additionally, samples which were prepared at 600°C in oxygen were allowed to cool and then flushed for 2 hr with a flow of methanol-saturated N_2 or a flow of H_2O-saturated N_2. Finally, certain samples which were prepared at 600°C in oxygen were simply allowed to equilibrate with room-temperature moisture over a period of several weeks in the laboratory.

RESULTS

The electronic absorption spectrum of 0.5% Cu/Al_2O_3, which has been freshly prepared from thermal decomposition of $Cu(NO_3)_2$ on γ-Al_2O_3 in either flowing oxygen or in vacuum, is shown as A in Fig. 1. It consists of a very broad asymmetrical band centered at approximately 13,500 cm^{-1}. If one allows this freshly prepared material to equilibrate exposed to ambient moisture, a gradual transformation occurs over a period of approximately 2 weeks. The equilibrated sample has an optical spectrum shown as B in Fig. 1. The optical spectrum of this sample was identical to that of the sample prepared more quickly in a flow of H_2O-saturated N_2. Although there are gross similarities in band position with the freshly prepared spectrum A, the reduction in intensity throughout the spectral scan stands out clearly. There are not sufficient differences in the methanol-equilibrated sample relative to the H_2O-equilibrated sample to justify its inclusion in Fig. 1 other than its intensity throughout lies between the two samples described above.

The peculiar shape of the electronic absorption spectra in the 7000-cm^{-1} regime needs further comment. It is well known that one of the vibrational overtones of the hydroxyl group occurs in this energy re-
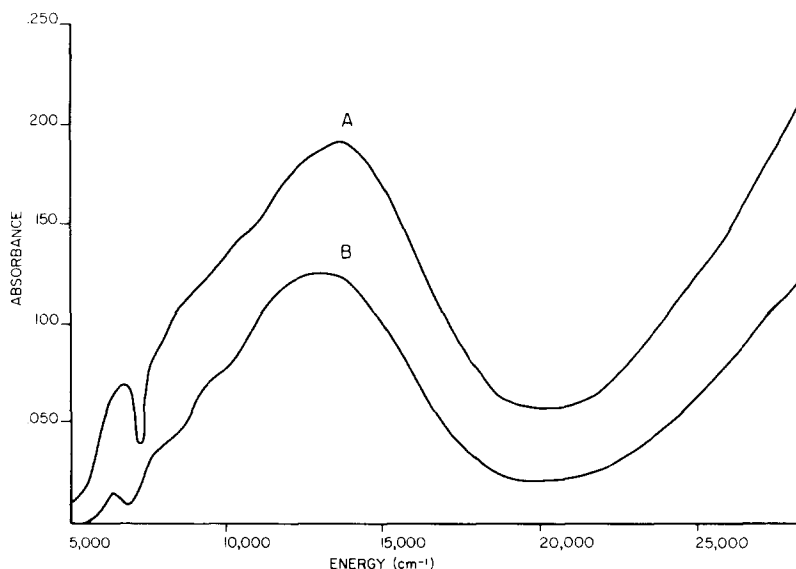

Fig. 1. Electronic absorption spectra (obtained from reflectance spectra through the use of Melamed's conversion procedure) of freshly prepared 0.5% Cu/Al_2O_3 (spectrum A) and of the same sample which was allowed to equilibrate in the laboratory (spectrum B).

gion. This can be confirmed by recording the spectrum of γ-Al_2O_3 versus $BaSO_4$. Consequently the observed absorbance minimum in the 7000-cm^{-1} regime for the Cu/Al_2O_3 sample is largely a result of the differential number of surface hydroxyl groups on this sample relative to the reference γ-Al_2O_3 (prepared simultaneously with the Cu/Al_2O_3 sample). Partly because of this unusual shape, a nonlinear least-squares fit of the spectral data to a set of Gaussians did not result in a unique solution, especially in the broad spectral range between approximately 7000 and 11,000 cm^{-1}. However, one can confidently center a broad Gaussian at 13,500 cm^{-1} as well as one in the 6500-cm^{-1} regime for both samples.

It is evident from Fig. 1 that there are no absorption maxima in the regime 18,000–25,000 cm^{-1}, an implied assumption made as a result of Berger and Roth's (3) calculation of the bonding parameters (vide infra). However, both samples have a maximum at approximately 39,000–40,000 cm^{-1}. The intensity differences between the two samples persist into the uv spectra range.

When the EPR spectrum of freshly prepared material (either in oxygen or in vacuum at 600°C) is taken at 77°K, the appropriate spin-Hamiltonian parameters, $A_\parallel$, $g_\parallel$, and $g_\perp$, can be measured and are collected in Table 1. It was felt that little improvement in these values would be achieved

through spectral simulation, especially because of an obvious underlying isotropic spectrum centered around $g = 2.15$ and its complicating effects in the $g_\perp$ regime. Furthermore, it is noted that no resolved hyperfine splitting is evident on the $g_\perp$ component.

Significant change is apparent in the spectrum obtained from the H_2O-equilibrated sample when it is examined at 77°K. (It should be reemphasized that there are no differences between the spectrum resulting from room-temperature equilibration in the lab environment and a sample equilibrated in a H_2O-saturated stream of N_2.) If the spin-Hamiltonian parameters are collected again by inspection and included in Table 1, it can be seen that there are significant changes in both $A_\parallel$ and $g_\parallel$. The parallel hyperfine splitting has gotten significantly smaller compared to the freshly prepared material. The parallel g tensor has gotten significantly larger.

If the freshly prepared sample is equilibrated in a methanol-saturated stream of N_2 there are significant changes in both $A_\parallel$ and $g_\parallel$. These values are presented in Table 1 and are seen to lie between the freshly prepared material and the material equilibrated in H_2O.

For comparison the spin-Hamiltonian parameters for the impregnated air-dried $Cu(NO_3)_2$ on γ-Al_2O_3 are collected in Table 1 along with those for the $Cu(NO_3)_2$-

TABLE 1

g Values (± 0.001) and A Values (± 5 G)

Sample	$g_\parallel$	$g_\perp$	$A_\parallel$
0.5% Cu/Al_2O_3 (vacuum or O_2)	2.309	2.073	173×10^{-4} cm^{-1} (160 G)
0.5% Cu/Al_2O_3 (MeOH-equilibrated)	2.325	2.082	162×10^{-4} cm^{-1} (149 G)
0.5% Cu/Al_2O_3 (H_2O-equilibrated)	2.356	2.083	154×10^{-4} cm^{-1} (140 G)
0.5% $Cu(NO_3)_2/$ γ-Al_2O_3 (air-dried)	2.351	2.075	161×10^{-4} cm^{-1} (147 G)
0.5% $Cu(NO_3)_2/$ γ-Al_2O_3 (dried at 120°C)	2.350	2.075	161×10^{-4} cm^{-1} (147 G)

impregnated material which has been further dried at 120°C.

DISCUSSION

The model proposed for the freshly prepared, dehydrated surface of 0.5% Cu/Al_2O_3 is one in which the local site symmetry of the exposed surface copper ions is C_{4v}. On the other hand, the rehydrated surface finds the copper ions in essentially D_{4h} symmetry where the rehydrating moiety has capped the previously open octahedral (C_{4v}) site. This change in symmetry is the principal explanation for the intensity variation observed in the electronic absorption spectra. This can be explained by the mixing of metal $3d$ and ligand wavefunctions via the C_{4v} ligand field as Ballhausen and Liehr (9) demonstrated for tetrahedral molecules.

Certainly there are shifts in the positions of the underlying d–d transitions which constitute the broad asymmetric band of transitions in the regime 6000–15,000 cm^{-1}. However, the possibility of consistently sorting out these transitions through Gaussian deconvolution techniques in these particular spectra has failed. Furthermore, it has been adequately demonstrated through literature examples (10–12) that within this broad featureless spectral range several site symmetries may be accommodated with the appropriate ligand field transitions. In addition, at appropriate ligand distances, C_{4v} and D_{4h} can have identical transitions. On the other hand, the intensities of the transition should be different.

It is worth emphasizing that the expected effects of moisture on the reflectance spectra of porous surfaces, as carefully outlined by Kortüm and Braun (13), are exactly the reverse of those noted for the rehydration of the surface of 0.5% Cu/Al_2O_3. In other words, the reflectance results cannot simply be ascribed to differences in the refractive indices of the sample and surrounding scattering medium. Furthermore, experimentally no difference was noted in the refractive indices between the two samples.

Turning now to the EPR results, several detailed theoretical and experimental studies (14–21) of the effect of axial coordination on the behavior of the Cu(II) $3d$ levels in tetragonally distorted octahedral environments have revealed the following qualitative effects. There is an increase in the $g_{\parallel}$ values with axial ligand interaction while at the same time the corresponding copper hyperfine splitting decreases (i.e., $A_{\parallel}$ values shift in a positive direction). This can be predicted almost purely on electrostatic grounds.

These concepts find application in the present study and further substantiate the proposed model when the EPR spectra of freshly prepared or dehydrated 0.5% Cu/Al_2O_3 are compared with the spectrum of material which has been allowed to equilibrate with room moisture. In both cases the spectra are those resulting from a tetragonally distorted octahedron with a $d_{x^2-y^2}$ ground state since $g_{\parallel} > g_{\perp}$. Furthermore, if one treats the freshly O_2-prepared and vacuum-prepared samples as identical (a reasonable proposition considering the relatively poor oxidizing ability of O_2 relative to the strong oxidizing properties of NO_3^-) and both possess a single axial ligand, then the fully rehydrated sample has a ligand at the other previously vacated axial site. A reasonable test of ligand participation at this axial site would be to vary the base strength (as a reasonable measure of coordination strength) of the axial ligand and observe the effects of this coordination on $g_{\parallel}$ and $A_{\parallel}$. Since methanol is approximately a 100-fold-weaker base (and for this argument a weaker coordinating ligand) than water, the surface which is allowed to equilibrate in gaseous methanol should have $g_{\parallel}$ and $A_{\parallel}$ values intermediate between the dehydrated (vacuum) and rehydrated (H_2O) samples. This is precisely what is observed as seen from the results compiled in Table 1. The more basic solvent gave larger $g_{\parallel}$ values and smaller hyperfine interactions, which is at least in qualitative agreement with previous work and substan-

tiates the rehydration model proposed from the reflectance spectra observations.

Although in the past bonding information has been derived from similar studies (3, 22), the approximations involved in such considerations, combined with the lack of spectral resolution, especially in the $g_\perp$ region of the EPR spectra, argue strongly against such a derivation in this instance. However, it is worth noting that the bonding parameters previously derived (3) for the proposed C_{4v} site must be in error since that study required an electronic transition to the $d_{x^2-y^2}(E_e - E_{b1})$ level at 25,000 cm^{-1}. No such transition is evident in the present study. Furthermore, it is worth noting that the procedure used to calculate the bonding parameters generates an infinite set of solutions, all internally self-consistent. In other words one cannot fit both the bonding parameters and the transition energies from a knowledge of just the spin-Hamiltonian parameters.

In conclusion, it has been demonstrated through the complimentary use of electronic absorption spectra and EPR spectra that freshly prepared 0.5% Cu/Al_2O_3 has a significant number of C_{4v} sites which are available for rehydration. Upon axial rehydration, the site symmetry is changed to approximately D_{4h}, explaining the loss in intensity in the electronic absorption spectrum.

REFERENCES

1. Selwood, P. W., and Dallas, N. S., *J. Amer. Chem. Soc.* **70**, 2145 (1948).
2. Jacobson, P. E., and Selwood, P. W., *J. Amer. Chem. Soc.* **76**, 2641 (1954).
3. Berger, P. A., and Roth, J. F., *J. Phys. Chem.* **71**, 4307 (1967).
4. Lumbeck, H., and Voitländer, J., *J. Catal.* **13**, 117 (1969).
5. Lumbeck, H., and Voitländer, J., *Z. Phys. Chem. (Frankfurt am Main)* **79**, 225 (1972).
6. Deen, R., Scheltus, P. I., and DeVries, G., *J. Catal.* **41**, 218 (1976).
7. Friedman, R. M., Freeman, J. J., and Lytle, F. W., *J. Catal.* **55**, 10 (1978).
8. Melamed, N. T., *J. Appl. Phys.* **34**, 560 (1963).
9. Ballhausen, C. J., and Liehr, A. D., Jr., *Mol. Spectrosc.* **2**, 342 (1958).
10. Holmes, O. G., and McClure, D. S., *J. Chem. Phys.* **26**, 1686 (1957).
11. Dawson, K., Hitchman, M. A., Prout, C. K., and Rossotti, F. J. C., *J. Chem. Soc. Dalton Trans.*, 1509 (1972).
12. Hitchman, M. A., and Waite, T. D., *Inorg. Chem.* **15**, 2150 (1976).
13. Kortüm, G., and Braun, W., *Angew. Chem. Int. Ed. Engl.* **2**, 333 (1963).
14. Maki, A. H., and McGarvey, B. R., *J. Chem. Phys.* **29**, 31 (1958).
15. McGarvey, B. R., *J. Phys. Chem.* **60**, 71 (1956).
16. Kuska, H. A., Rogers, M. T., and Drullinger, R. E., *J. Phys. Chem.* **71**, 109 (1967).
17. Rogers, M. T., and Kuska, H. A., *J. Chem. Phys.* **43**, 1744 (1965).
18. Roos, B., *Acta Chem. Scand.* **20**, 1673 (1966).
19. Roos, B., *Acta Chem. Scand.* **21**, 1855 (1967).
20. Falk, K. E., Ivanova, E., Roos, B., and Vänngard, T., *Inorg. Chem.* **9**, 566 (1970).
21. Ammeter, J., Rist, G., and Gunthard, H. H., *J. Chem. Phys.* **57**, 3852 (1972).
22. Nicula, A., Stamires, D., and Turkevich, J., *J. Chem. Phys.* **42**, 3684 (1965).

D. B. LOSEE
A. J. KASSMAN
P. A. WILSON

Philip Morris Research
P.O. Box 26583
Richmond, Virginia 23261