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Preparation of Copper on Magnesia Catalysts: An Electron Spin Resonance Study

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When MgO powders are impregnated with copper ions dissolved in water, hydrolysis to $Mg(OH)_2$ takes place. Following decomposition of the latter, considerable loss of surface area occurs with incorporation of Cu^{2+} ions in the bulk of MgO, as revealed by ESR spectra. Impregnation with Cu^{2+} ions dissolved in organic solvents decreases the amount of Cu^{2+} ions incorporated into the bulk of MgO. These observations lead to a method of preparation of high surface area MgO powders with Cu^{2+} ions at their surface.

INTRODUCTION

That ESR can be a powerful tool in providing information on copper catalysts supported on alumina is evidenced by the studies of Matsunaga (*1*), Berger and Roth (*2*), and Lumbeck and Voigtländer (*3*). These studies led to the identification of isolated Cu^{2+} ions in open octahedral holes, a surface CuO phase in various states of dispersion, and the migration of isolated copper ions to form metallic clusters on reduction, followed by back-migration of the ions during reoxidation. These studies did not, however, attempt to correlate surface structure to catalytic activity.

An earlier attempt to correlate catalytic activity with the surface structure of Cu–MgO catalysts by Benson *et al.* (*4*) led to the assumption that catalytic sites for H_2–D_2 equilibration at 78 K consisted of surface O^- ion formed by electron capture: $O^{2-} + Cu^{2+} \rightarrow O^- + Cu^+$. However, the active sites responsible for the H_2–D_2 equilibration on MgO and Cu–MgO catalysts at 78 K were later found (*5*) to involve V_1 and V^*_{OH} paramagnetic centers (*6*), which did not require any copper in or on MgO. Nevertheless, the earlier work by Benson *et al.* (*4*) did stimulate a subsequent ESR study of the Cu^{2+} ions on Cu–MgO catalysts (*7*) which is reported in the present paper, and which can be related to the method of preparation and to the thermal and chemical history of the catalysts (*7*). Maksimov *et al.* (*8*) have also reported similar observations.

EXPERIMENTAL METHODS

Catalysts

Catalysts containing 5.0, 0.5, 0.05 and 0.005 mole% copper on MgO were prepared by impregnating the oxides with cupric nitrate solutions prepared by dissolving Asarco copper metal (99.999+% Cu, less than 1 ppm Ni) in Baker and Adamson reagent grade nitric acid (less than 0.05 ppm Ni). An excess of distilled water was used in all impregnations, including an MgO blank treated in water only. The reagent grade MgO from Mallinckrodt is denoted as M-MgO. When

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hydrolyzed and heated in air for 24 hr at 700 K, a high surface area MgO was obtained, HS-MgO. The catalysts were first evaporated to dryness in a double boiler, and then calcined in air at 700 K for 24 hr. This procedure hydrolyzed the MgO to its hydroxide prior to calcination. The formation of the hydroxide was verified by X-ray diffraction.

A 5.0 mole% copper on MgO catalysts was also prepared by impregnating MgO with Baker and Adamson Reagent cupric acetate (Cr, Co, and Ni less than 15 ppm) in ethanol solution. This catalyst was also evaporated on a double boiler and calcined at 700 K in air for 24 hr. The ethanol was used as a solvent to prevent extensive hydrolysis of the MgO. This catalyst is denoted by the suffix -EA, denoting ethanol-acetate. No hydroxide phase was detected by X-ray diffraction following the evaporation of the ethanol solvent.

Catalysts containing 5.0, 0.5, and 0.05 mole% copper on MgO were heated at 1300 K for 15 hr in air to obtain solid solutions.

Specific surface areas were measured by the nitrogen BET method at liquid nitrogen temperature. Specific surface areas were also calculated from the volume-average crystallite dimensions obtained by X-ray line broadening. Smooth, compactly shaped crystallites were assumed.

ESR and XPS Studies

ESR spectra were obtained using a VARIAN E-3 spectrometer operating in the *X*-band with a modulation frequency of 100 kHz. Microwave power levels and modulation amplitudes were kept low enough to avoid saturation and/or distortion of the resonance. Spectra were recorded at about 293 and 80 K, the latter by using a liquid nitrogen dewar insert. The powder catalysts were contained in 4 mm o.d.-3 mm i.d. quartz tubes. Pretreatments were carried out by fusing the sample tubes to a high vacuum manifold using graded seals. Following pretreatment, the tubes were sealed *in vacuo* and transferred to the ESR spectrometer.

Spin density and *g*-values estimates were obtained by using the Cr^{3+} impurity line in the MgO and DPPH taped to the quartz dewar. The derivative spectra were doubly integrated numerically using the method described by Poole (*9*).

X-Ray photoelectron spectra (XPS) of some of our Cu–MgO catalysts were taken by W. N. Delgass at the Lawrence Radiation Laboratory, University of California, Berkeley. They have been discussed in detail in a separate publication (*10*).

RESULTS

Surface Areas

Specific surface areas for some of our catalysts are presented in Table 1. Straight BET plots were obtained for all samples. There was negligible hysteresis for an adsorption–desorption isotherm at liquid nitrogen temperature for the high surface area MgO catalyst, HS-MgO. Specific surface areas calculated from volume-average crystallite sizes obtained by X-ray line

TABLE 1

SPECIFIC SURFACE AREAS ($m^2 g^{-1}$)

Sample	N_2 BET	X-ray line broadening
M-MgO	21	16.6
HS-MgO		
calcined	138	114
0.005% Cu-MgO		
calcined	143	114
0.05% Cu-MgO		
calcined	126	93
0.5% Cu-MgO		
calcined	27	24.5
5.0% Cu-MgO		
calcined	18	23.2
M-MgO (treated in HNO_3)	7.7	—
5.0% Cu-MgO-EA	17	—
0.05% Cu-MgO (solid solution)	31	—
0.5% Cu-MgO (solid solution)	16	—
5.0% Cu-MgO (solid solution)	2.4	—

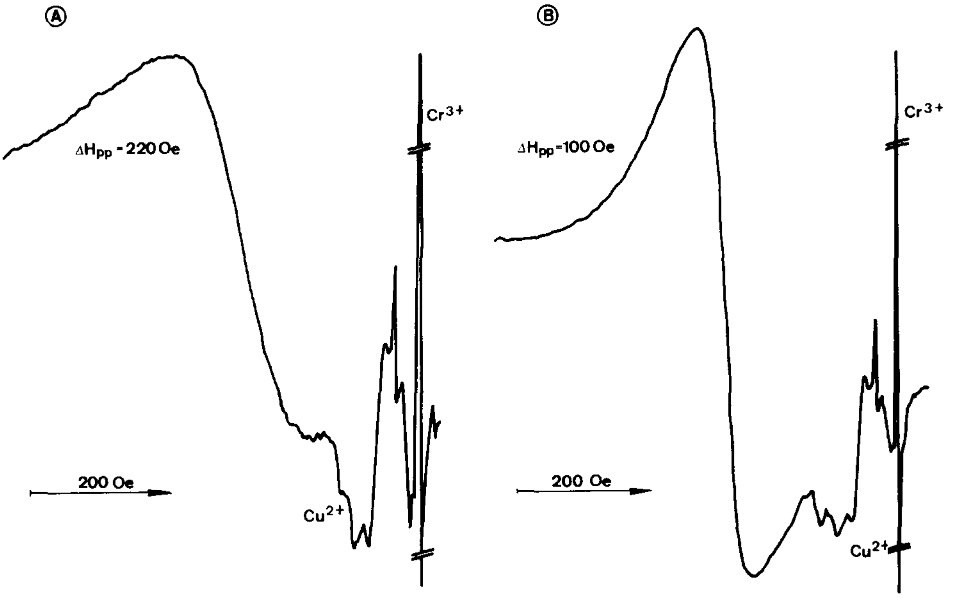

FIG. 1. ESR spectrum of 5.0% Cu-MgO-EA catalyst evacuated 12 hr at 800 K. (A) 293 K, gain = 6.2×10^4, modulation amplitude = 5 Oe; (B) 77 K, gain = 2.0×10^4, modulation amplitude = 5 Oe.

broadening are also presented in Table 1. Agreement between specific surface areas obtained by nitrogen BET and X-ray line broadening for MgO has also been reported by Anderson and Horlock (*11*) and Kotera *et al.* (*12*). It demonstrates that changes in specific surface areas are due exclusively to changes in average crystallite size.

ESR and XPS Results

Some typical ESR spectra of our Cu–MgO catalysts are reproduced in Figs. 1–5. The most obvious feature of these

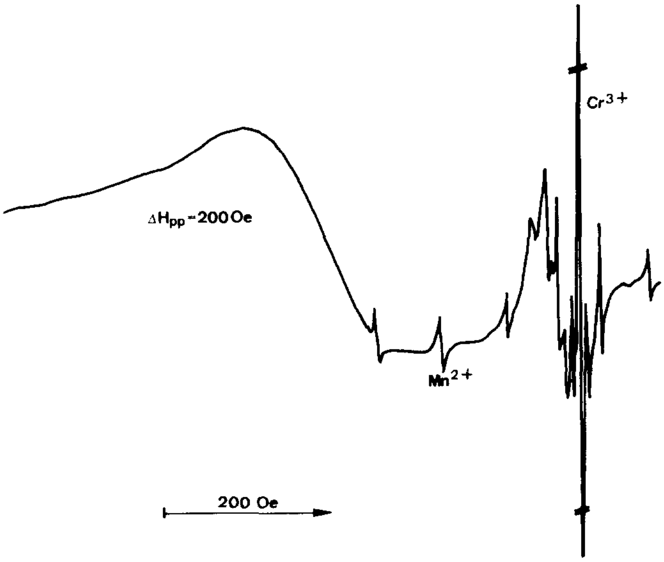

FIG. 2. ESR spectrum of 5.0% Cu-MgO-EA catalyst reduced in H_2 for 12 hr at 800 K. Gain = 1.25×10^5, modulation amplitude = 1 Oe, temperature = 293 K.

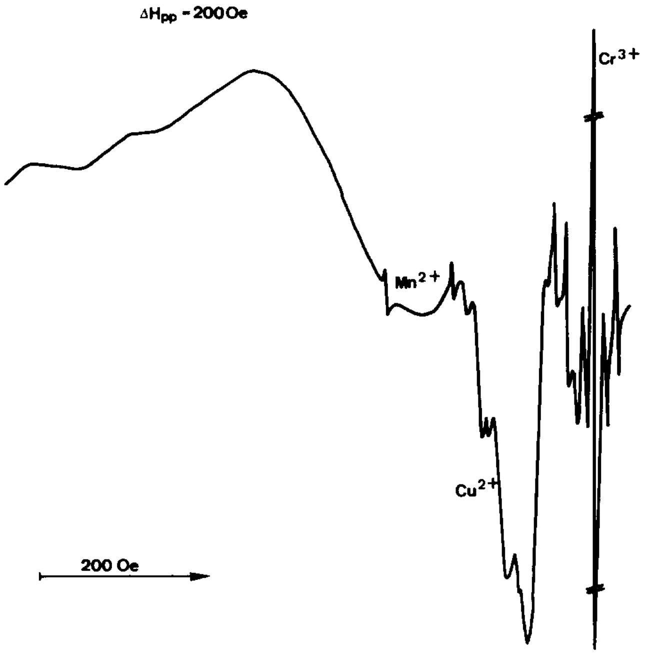

FIG. 3. ESR spectrum of 5.0% Cu-MgO-EA catalyst, reduced, and reoxidized with O_2 (50 Torr) for 12 hr at 293 K at 12 hr at 800 K. Gain = 1.25 × 10^5, modulation amplitude = 1 Oe, temperature = 293 K.

spectra is the presence of two overlapping ESR signals, a symmetric line at $g = 2.192 \pm 0.002$ of relatively high intensity and a smaller intensity anisotropic line characterized by the following g-values: $g_{\parallel} = 2.35$–2.44 and $g_{\perp} = 2.06$.

The symmetric line corresponds to Cu^{2+} ions replacing Mg^{2+} ions in the MgO lat-

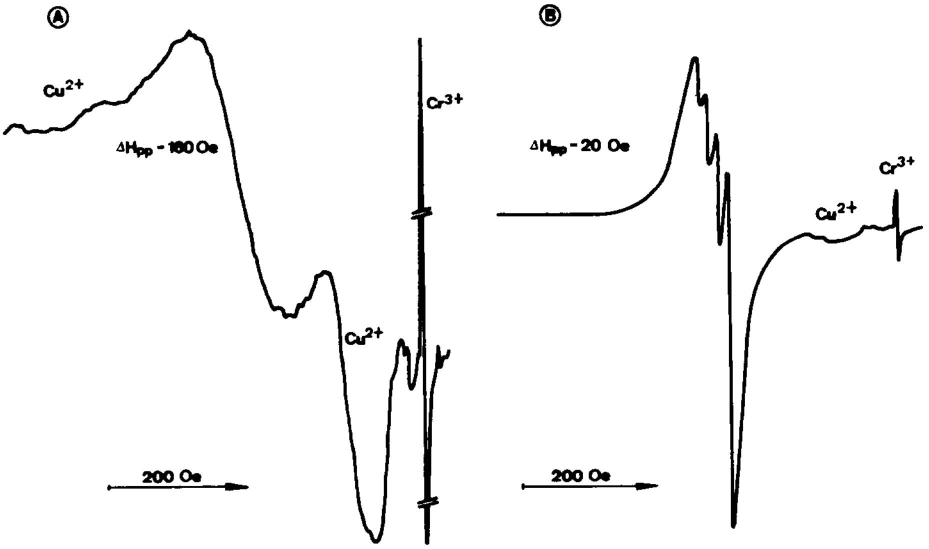

FIG. 4. ESR spectrum of 0.05% Cu-MgO solid solution. (A) 293 K, gain = 3.2 × 10^4, modulation amplitude = 5 Oe; (B) 77 K, gain = 8.0 × 10^3, modulation amplitude = 1 Oe.

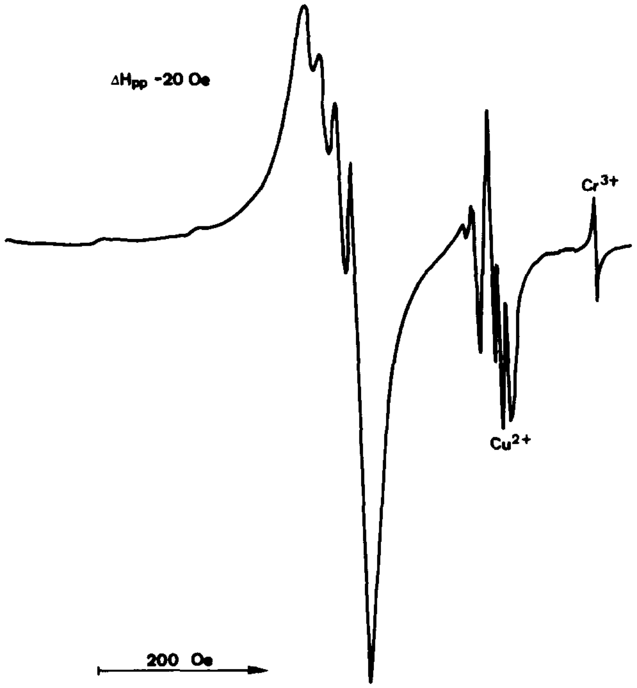

FIG. 5. ESR spectrum of 0.05% Cu-MgO solid solution evacuated for 10 hr at 1200 K. 77 K, gain = 8.0 × 10^3, modulation amplitude = 1 Oe.

tice (*13–15*), while the anisotropic line is characteristic of Cu^{2+} ions in tetragonal symmetry, i.e., Cu^{2+} ions at the surface of MgO.

In some spectra, which are not shown, the symmetric Cu^{2+} line was observed to exhibit strong dipolar broadening that prevented an accurate evaluation of its intensity. However, for most cases, it was possible to doubly integrate the ESR spectra; Table 2 reports spin density estimates for this particular line in a variety of Cu–MgO catalysts, either after calcination at 800 K or after firing in air at 1300 K. In the latter case, a solid solution of Cu^{2+} in MgO was obtained. The accuracy of the spin density values listed in Table 2 is estimated to be of ±50%.

A comparison of the spectra recorded at 80 and 293 K shows that the intensity of

TABLE 2

ESTIMATED SPIN DENSITIES FOR THE SYMMETRIC Cu^{2+} LINE IN Cu–MgO CATALYSTS[a]

Catalyst	Calcined at 800 K	Solid solution[b]	Calculated[c]	ΔCu^{2+} [d]	% Cu^{2+} (surface)[e]
0.05% Cu–MgO	6.8×10^{18}	7.8×10^{18}	7.1×10^{18}	1.0×10^{18}	12.7
0.5% Cu–MgO	5.7×10^{19}	7.8×10^{19}	7.1×10^{19}	2.1×10^{19}	26.7
5.0% Cu–MgO	4.3×10^{20}	7.9×10^{20}	7.4×10^{20}	3.6×10^{20}	45.5
5.0% Cu–MgO–EA	0.2×10^{20}	7.9×10^{20}	7.4×10^{20}	$7.7 \times 10\ ^{0}$	97.5

[a] Spin densities in spins g^{-1}.
[b] Fired at 1300 K for 15 hr.
[c] Assuming that all the copper is as paramagnetic Cu^{2+} ions.
[d] Difference between solid solution and calcined catalyst.
[e] % Cu^{2+} at the surface after calcination at 800 K.

the Cu^{2+} symmetric line follows the Curie law; hence, his resonance is due to fairly diluted Cu^{2+} ions in the MgO matrix. However, the narrowing of this line at 80 K, eventually leading to the resolution of the Cu nucleus hyperfine structure ($I_{Cu} = 3/2$, 4 hyperfine lines), indicates that dipolar broadening is strongly affecting the lineshape. This effect must be expected, as, for a 5.0 mole Cu^{2+} solid solution in MgO, the average Cu–Cu distance is of about 7 Å. The corresponding values for the 0.5 and 0.05 mole% Cu^{2+} solid solutions in MgO are, respectively, of 18 and 37 Å. From these evaluations, antiferromagnetic type interactions between Cu^{2+} ions can be safely rejected, as these would only occur for Cu–Cu distances smaller than 2.5 Å.

The spin Hamiltonian of bulk Cu^{2+} species in MgO is simply given by:

$$H = g\beta\,\mathbf{H}\cdot\mathbf{S} + \mathbf{A}\mathbf{I}\cdot\mathbf{S}, \qquad (1)$$

as the Cu^{2+} ions are in a regular octahedral environment. The observation of Cu^{2+} ions in such a regular symmetry is made possible through a dynamic Jahn-Teller effect and the observed parameters, g-value (2.192) and the hyperfine splitting ($A_{Cu} =$ 19 Oe, see Figs. 4B and 5 for the 0.05 mole% Cu^{2+} catalysts), are in excellent agreement with values reported for dilute Cu^{2+} ions in MgO single crystals (*13,15*).

As shown by Figs. 1A and 2, the bulk Cu^{2+} ion spin density is not affected by reduction in hydrogen at 800 K. Some increase in this spin density has sometimes been experienced on heating the 5.0 mole% Cu–MgO–EA catalyst to 800 K; it is probably due to further incorporation of surface Cu^{2+} ions in the bulk after the 700 K calcination.

The spin Hamiltonian of the axially symmetric Cu^{2+} species, is given by:

$$H = \beta(g_{\|}H_zS_z + g_{\perp}(H_xS_x + H_yS_y)) + A_{\|}S_zI_z + A_{\perp}(S_xI_x + S_yI_y), \qquad (2)$$

where all the parameters have their usual meaning.

Table 3 summarizes some typical values of the characteristic ESR parameters, g_{av} being defined as $g_{av} = (1/3)(g_{\|} + 2g_{\perp})$.

The values we report for the axially symmetric Cu^{2+} ions are close to those reported for Cu^{2+} ions on Linde Y zeolite (*16*), acetylacetonatocopper on SiO_2 (*17*), Cu^{2+} on Dowex resins (*18*), and Cu^{2+} ions on alumina (*1*). Similar values were also found in a variety of other materials. The occasional observation of an additional hyperfine feature on the high field side of the spectra, in this study as well as in the previous work of Matsunaga (*1*), is explained by an angular anomaly in the ESR powder spectrum, i.e., the presence of the so-called "extraneous line" discussed in the former work of Neiman and Kivelson (*19*).

The freshly impregnated 0.05 mole%

TABLE 3

TYPICAL ASYMMETRIC Cu^{2+} LINE ESR PARAMETERS (293°K)

Catalyst	$g_{\|}^{a}$	$g_{\perp}^{a}$	g_{av}^{a}	$A_{\|}^{b}$(cm^{-1})	$A_{\perp}^{c}$(cm^{-1})
0.05% Cu–MgO (freshly impregnated, $Mg(OH)_2$)	2.352	2.065	2.161	0.012	0.0013
0.05% Cu–MgO (solid solution, evacuated at 1200 K for 10 hr)	2.365	2.057	2.160	0.011	0.0016
5.0% Cu–MgO–EA (evacuated at 800 K)	2.438	2.060	2.186	0.0135	—

[a] All g-values at ±0.003.

[b] $A_{\|}$-values at ±0.003.

[c] $A_{\perp}$-values at ±0.0001.

Cu–MgO catalyst did not show a symmetric Cu^{2+} line, but only the anisotropic spectrum. Hence, almost all the Cu^{2+} ions, in this particular sample, sit in an axially symmetric environment, probably at the surface and certainly in a superficial layer of $Mg(OH)_2$. X-Ray diffraction data verified the existence of this hydroxide layer before calcination at 700 K.

As shown in Figs. 1 to 3, the intensity of the anisotropic Cu^{2+} line is reduced by H_2 at 800 K (Fig. 2) and regenerated by exposure to O_2 (Fig. 3). This shows that the axially symmetric Cu^{2+} ions are accessible and on the surface and not associated with bulk axial defects sites. The most active catalyst, 5.0 mole% Cu–MgO–EA, contains also more axially symmetric surface Cu^{2+} ions than any other Cu–MgO catalyst. It may be interesting to note that, in addition to the disappearance of the surface Cu^{2+} line upon reduction, the typical ESR pattern of Mn^{2+} ions in regular octahedral environment shows up. This indicates that before reduction, manganese as an impurity was present in the samples, probably in a valence state not observable by ESR at 77 K or above, i.e., Mn^{3+}. This particular behavior of manganese in MgO has recently been reported for the Mn–MgO system (*33*).

XPS spectra of the same systems have been discussed in another publication (*10*). They support our results on the variation in composition and oxidation state of the surface Cu^{2+} species.

DISCUSSION

The variation in the surface areas of the Cu–MgO catalysts prepared by aqueous impregnation is interesting. The MgO is hydrolyzed to $Mg(OH)_2$, and the decomposition of the $Mg(OH)_2$ leads to the formation of MgO with varying crystallite sizes depending on the amount of $Cu(NO_3)_2$ present.

Various authors (*11, 20–30*) have discussed the decomposition of $Mg(OH)_2$. At low temperature, such as we used, H_2O is removed from the hydroxide with the formation of a large number of MgO nuclei. Because the oxide lattice of MgO is not too different from that of $Mg(OH)_2$, the decomposition is nearly topotactic and extensive migration of ions to provide for the growth of large crystallites does not occur. This leads to a low density, highly strained, high surface area MgO containing residual bulk and surface hydroxyl groups. This form of MgO readily readsorbs water. Heating to about 1300 K leads to well-formed MgO crystallites which readsorb H_2O very slowly.

The presence of the $Cu(NO_3)_2$, and more generally of the nitrate ion, increases the rate of growth of the crystallites and leads to a lower surface area MgO product. The addition of HNO_3 to MgO powder, followed by calcining at 700 K in air, lowers the specific surface area from 21 to 7.7 $m^2\ g^{-1}$. Cupric ions in the MgO lattice also enhance sintering. This effect is more clearly demonstrated by the surface areas of the Cu–MgO solid solutions containing, respectively, 0.05, 0.5 and 5.0 mole% copper. After heating at 1300 K for 15 hr in air, the final specific surface areas show an appreciable decrease with increasing copper concentrations.

A comparison of ESR spectra of the bulk Cu^{2+} ions for the aqueous Cu–MgO and the Cu–MgO solid solutions at 80 K shows that the Cu^{2+} ion lines become much narrower for the solid solutions, especially as the Cu^{2+} concentration decreases. The sharp decrease in line width at 80 K is due to an increase in spin–spin relaxation time, T_2, for solid solutions. This indicates the presence of dipolar broadening of the lines and that the bulk Cu^{2+} ions are not well dispersed in the Cu–MgO catalysts following calcination. Taylor (*31*) has reported that even coprecipitated copper hydroxide–magnesium hydroxide catalysts are not homogeneous. This implies that while Cu^{2+} ions are incorporated into the $Mg(OH)_2$ during impregnation in water, they are not evenly distributed in the lattice. The Cu–MgO formed by decomposition of $Cu(OH)_2$–$Mg(OH)_2$ ions also contains Cu^{2+} ion clusters, as shown by the fact that the line width of the symmetric Cu signal is independent of the copper content, at constant temperature. These Cu^{2+} ions become evenly distributed upon heating to 1300 K for 15 hr. These conditions are sufficient to incorporate up to 20 mole% Cu^{2+} in MgO as a solid solution (*32*), which is in agreement with the observation of Maksimov *et al.* (*8*).

Table 2 gives the difference between the number of Cu^{2+} ions, per gram of catalyst, observed by ESR for Cu–MgO solid solutions and the number observed for the symmetric Cu^{2+} signal in four different Cu–MgO catalysts. These are denoted by ΔCu^{2+} in Table 2. While the measured values for Cu^{2+} ion spin densities involve about a 50% absolute uncertainty, the values for the solid solutions are at most only 10% higher than the actual number of copper atoms present in the 5.0, 0.5, and 0.05% Cu–MgO solid solutions. This agreement, along with the fact that the ΔCu^{2+} values are obtained by subtracting numbers obtained using the same method for their measurement, gives these ΔCu^{2+} values meaning. Going one step further, we may assume that the ΔCu^{2+} values correspond to the copper which is at the catalyst surface and to calculate the percentage of surface Cu^{2+} ions in the various catalysts.

ESR spectra also show that the surface Cu^{2+} ions can be reduced in H_2 and easily reoxidized in O_2. This indicates that they can accept electrons readily and that they do not migrate along the surface to form metallic clusters. If they did, exposure to O_2 would not restore the axially symmetric Cu^{2+} line, but would produce Cu_2O or CuO instead. Cu_2O is diamagnetic and CuO is antiferromagnetic. Except for small effects observed for nonstoichiometric compositions, neither have spin paramagnetism.

ESR lines for the axially symmetric Cu^{2+} species are relatively narrow. This indicates that these surface Cu^{2+} ions are isolated from each other. It is therefore likely that these Cu^{2+} ions are reduced, possibly to Cu^{+}, and reoxidized without migration because migration of reduced copper species would lead to clustering.

The 5.0 mole% Cu–MgO–EA must contain CuO or an antiferromagnetic surface phase rich in copper to account for the fact that the total spin densities for both species are too small to account for all the copper which is present. CuO on the 5.0% Cu–MgO–EA catalyst is reduced to metallic copper in H_2 at 800 K. Traces of metallic copper on the walls of the reactor have been observed downstream from the catalyst following reduction in flowing H_2 at 800 K. In addition, X-ray diffraction spectra show small amounts of CuO following calcination and small amounts of copper metal after reduction in H_2 at 800 K.

CONCLUSIONS

Two major observations are of general interest in catalyst preparation. First, quantitative ESR spectroscopy has shown that for Cu^{2+} concentrations up to 5.0 mole% most of the Cu^{2+} ions will be present in the bulk of the MgO crystallites if the MgO is hydrolyzed to $Mg(OH)_2$ in aqueous Cu^{2+} solutions. On the other hand, if the MgO is not extensively hydrolyzed during the impregnation, the Cu^{2+} ions can be largely concentrated on the surface of the MgO crystallites.

Second, the incorporation of Cu^{2+} ions into the $Mg(OH)_2$ leads to increased crystallite size of MgO after decomposition of the $Mg(OH)_2$. This is due to either a change in the topotactic process by which

$Mg(OH)_2$ is converted to MgO during dehydration, or to Cu^{2+} enhanced crystallite sintering, or both. The decrease in the specific surface areas during the formation of Cu–MgO solid solutions indicates that higher concentrations of Cu^{2+} ions does lead to higher rates of crystallite sintering.

ESR and XPS spectra show that paramagnetic Cu^{2+} ions on MgO can be reduced in H_2. ESR also shows that this reduction is reversible with O_2 and that only Cu^{2+} ions on the surface show changes with H_2 and O_2. The 5.0%, Cu–MgO–EA catalysts have much less copper inside the MgO crystallites and more copper at the MgO surface than the 5.0% Cu–MgO catalyst prepared by hydrolyzing MgO to $Mg(OH)_2$. We believe that the surface copper changes from Cu^{2+} to Cu^{+} ions during reduction in hydrogen. This is because the reduced state can be reoxidized to the previous state by treatment with oxygen. If metallic copper were the reduced state, it would be expected to migrate and form metallic clusters. These would reoxidize to diamagnetic Cu_2O or more probably to antiferromagnetic CuO, neither of which would give back the characteristic asymmetric spectra due to surface Cu^{2+} ions.

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REFERENCES

1. Matsunaga, Y., *Bull. Chem. Soc. Jap.* **34,** 1291 (1961).
2. Berger, P. A., and Roth, J. F., *J. Phys. Chem.* **71,** 4307 (1967).
3. Lumbeck, H., and Voigtländer, J., *J. Catal.* **13,** 117 (1969).
4. Benson, J. E., Walters, A. B., and Boudart, M., *J. Phys. Chem.* **72,** 4587 (1968).
5. Boudart, M., Delbouille, A., Derouane, E. G., Indovina, V., and Walters, A. B., *J. Amer. Chem. Soc.* **94,** 6622 (1972).
6. Derouane, E. G., Indovina, V., Walters, A. B., and Boudart, M., *in* "Proceedinns of the 7th International Symposium Reactivity of Solids, 1972" (F. S. Stone, M. W. Roberts and P. Anderson, Eds.), pp. 703–716. Chapman & Hall, London, 1972.
7. Walters, A. B., PhD dissertation, Stanford, 1970.
8. Maksimov, N. G., Chigrina, V. A., Boreskov, G. K., Anufrienko, V. F., and Yur-eva, T. M., *Kinet. Katal.* **13,** 446 (1972).
9. Poole, C. O., Jr., "Electron Spin Resonance." Wiley (Interscience), New York, 1967.
10. Delgass, W. N., Hughes, T. R., and Fadley, C. S., *Catal. Rev.* **4,** 179 (1970).
11. Anderson, P. J., and Horlock, R. F., *Trans. Farady Soc.* **58,** 1993 (1962).
12. Kotera, Y., Saito, T., and Terada, M., *Bull. Chem. Soc. Jap.* **36,** 195 (1963).
13. Orton, J. W., *Rep. Progr. Phys.* **22,** 204 (1959).
14. Orton, J. W., Auzins, P., Griffiths, J. H. E., and Wertz, J. E., *Proc. Phys. Soc., London* **78,** 554 (1961).
15. Coffman, R. E., *J. Chem. Phys.* **48,** 609 (1968).
16. Nicula, A., Stamires, D., and Turkevich, J., *J. Chem. Phys.* **42,** 3684 (1965).
17. Kavalerova, E. V., Golubev, V. B., and Evdokimov, V. B., *Russ. J. Phys. Chem.* **37,** 116 (1963).
18. Heitner-Wirguin, C., and Cohen, R., *J. Phys. Chem.* **71,** 2556 (1967).
19. Neiman, R., and Kivelson, D., *J. Chem. Phys.* **35,** 156 (1961).
20. Livey, D. T., Wanklyn, B. M., Hewitt, M., and Murray, O., *Trans. Brit. Ceram. Soc.* **56,** 217 (1957).
21. Roy, D. M., and Roy, R. R., *Amer. J. Sci.* **255,** 574 (1957).
22. Razouk, R. I., and Mikhail, R. S., *J. Phys. Chem.* **61,** 886 (1957).
23. Razouk, R. I., and Mikhail, R. S., *J. Phys. Chem.* **63,** 1050 (1959).
24. Meyer, J. W., and Yang, J., *Amer. J. Sci.* **260,** 707 (1962).
25. Horlock, R. F., Morgan, O. L., and Anderson, P. J., *Trans. Faraday Soc.* **59,** 721 (1963).
26. Weber, J. N., and Roy, R., *Amer. J. Sci.* **263,** 668 (1965).
27. Cimino, A., Porta, P., and Valigi, M., *J. Amer. Ceram. Soc.* **49,** 152 (1966).
28. Nielsen, T. H., and Leipold, N. H., *J. Amer. Ceram. Soc.* **49,** 626 (1966).

29. Freund, F., *J. Amer. Ceram. Soc.* **50,** 493 (1967).
30. Librant, Z., and Pampuch, R., *J. Amer. Ceram. Soc.* **51,** 109 (1968).
31. Taylor, E. H., *J. Amer. Chem. Soc.* **63,** 2906 (1941).
32. Schmitz-Dumont, O., and Fendel, H., *Monatsch. Chem.* **96,** (1965).
33. Derouane, E. G., and Indovina, V., *Bull. Soc. Chim. Belg.* **82,** 645 (1973).