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ABSTRACT

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It has been determined that about 5% of carbon monoxide gas which adsorbs on degassed magnesium oxide is in a paramagnetic state. Magnesium oxide was degassed at 850° C and 10^{-5} torr for 16 hours, cooled to room temperature, and then exposed to 150 torr of high-purity carbon monoxide. The resulting paramagnetic spectrum grew slowly for several weeks.

This paper describes the spectrum of the adsorbed CO radical ($g_{\parallel} = 2.0021$, $g_{\perp} = 2.0055$, $A_{\parallel} = 27.2$ gauss, $A_{\perp} = 8.8$ gauss, $A_{iso} = 15$ gauss), the probable type of site on which the molecule is adsorbed, its bonding, and the effect of evacuating at elevated temperatures. Author

INTRODUCTION

The adsorbed CO molecule as an intermediate species in heterogeneous catalysis plays an important role in such reactions as the Fisher-Tropsch process. The nature of CO adsorption on solid surfaces has been studied extensively in the last few years, primarily by infrared methods.[1] Interpretations of the data acquired by the infrared technique have not, however, been in agreement.[1,2] Blyholder[2] recently postulated that CO adsorption on metals is similar to the formation of metal carbonyls as

[redacted]

outlined by Orgel[3], and that the adsorption may be considered in view of molecular orbital theory. This reaction of CO with a suitable metal atom results in an unpaired electron in the antibonding π-molecular orbital on the carbon monoxide ligand.

Electron paramagnetic resonance (EPR) evidence to be presented in this paper indicates that part of the CO which adsorbs on well degassed MgO contains an unpaired electron in a π-molecular orbital on the carbon monoxide.

EXPERIMENTAL

Three types of magnesium oxide were used and were designated MgO I, MgO II, and MgO III. The first type, MgO I, was prepared from reagent-grade powder and contained about 0.001 percent Fe. The other types, MgO II and MgO III, were prepared from the same reagent-grade powder, which was impregnated with $FeCl_3$ to a total of 0.006 and 0.06 percent Fe, respectively. The powders were boiled in water for several hours, extruded into pellets with a hypodermic syringe, and dried in air at 100° C. Degassing was carried out by heating the pellets to 800° C in a vacuum for 16 hours. The BET surface area that was measured on one sample of MgO I after this treatment was 170 m^2/g.

The $C^{12}O$ used to obtain most of the data was purchased from a commercial source (99.5% minimum purity) and was used without further treatment. For one sample, $C^{12}O$ was prepared by reducing CO_2 with zinc. This technique was also used to produce a mixture of $C^{13}O$ and $C^{12}O$ from 57 percent $C^{13}O_2$ and 43 percent $C^{12}O_2$. The CO_2 was first frozen at -196° C, and the O_2 or other residual gases were removed by evacuation; then the gas was heated for several hours at 550° C in the presence of a zinc film. A mixture of

53 percent $C^{13}O$ and 47 percent $C^{12}O$ was also obtained from a commercial source. This gas was purified by contacting it with a zinc film at 400° C and removing condensable gases with a cold trap at -196° C. The carbon monoxide was admitted onto the sample at room temperature and at pressures ranging from 1 to 150 torr.

A conventional EPR spectrometer which operated at a cavity resonance frequency of 9.1 k Mc/sec (X-band) or 35 k Mc/sec (K-band) was used to obtain the data. The X-band cavity was a TE 102 mode type, while the K-band cavity was a right circular cylinder resonant in the TE 011 mode. A nuclear-magnetic-resonance-type gauss meter was used to monitor the magnetic field. The g-values were obtained by comparison with the value for α,α-diphenyl β-picryl hydrazyl ($g = 2.0036$) and with the value for the Cr^{+3} impurity ($g = 1.9797$) which is present in all samples studied. The number of spins associated with a particular line was determined by numerically integrating the derivative spectrum and comparing with a standard of pitch in KCl. The estimated error is ±30%. Relative intensities of the same line were determined by measuring the peak height. A spectrum of the sample was obtained soon after the carbon monoxide was admitted and at other specified times.

RESULTS

Upon exposure of the degassed MgO to $C^{12}O$, the X-band spectrum shown in Fig. 1 was observed. The spectrum grew in intensity for about 20 days. The rate of growth as well as the final intensity of the spectrum increased with the iron content of the sample (though not linearly). After 20 days the intensity of the spectra for MgO I, MgO II, and MgO III was in the ratio of 1.0:1.6:2.0. While the X-band spectrum of the evacuated MgO has no background lines at the magnetic fields of interest, the K-band spectrum showed an interfering line, which is believed to be the spectrum of Fe^{+3} ions.[4] This line appeared at the higher frequencies because the sensitivity of the instrument is more than an order of magnitude greater in this region, and the polycrystalline Fe^{+3} line is reduced in width while the CO line becomes broader. Since the total number of spins contributing to the CO and the iron lines is independent of frequency, the amplitude of the lines must correspondingly increase or decrease. In Fig. 2 the iron spectrum has been subtracted to give the resulting K-band $C^{12}O$ spectrum. Two of six Mn^{+2} lines are also shown in the figure. The g-values for the X-band and K-band spectra are listed in Table I. The EPR transition begins to saturate at approximately 1 mW of microwave power.

With the $C^{13}O$ - $C^{12}O$ mixture on the sample the spectrum at X-band is shown in Fig. 3. Of particular interest are the hyperfine lines, which are symmetrically disposed on each side of the $C^{12}O$ spectrum. In Fig. 3 the overlapping $C^{12}O$ spectrum is subtracted from the high field side so that the $C^{13}O$ spectrum can be clearly displayed. Values for the hyperfine coupling constants are listed in Table II. The other line with $g = 2.0080$ has not been identified. It was at first believed to be an impurity in the $C^{13}O$ - $C^{12}O$ mixture; however, several observations indicate otherwise. The low field line grew at the same rate and was removed at the same rate as the $C^{12}O$ line. Furthermore, the ratio of intensities remained the same whether the starting gas was purified CO or was made from CO_2. The fact that the unknown line was not present in the $C^{12}O$ made from CO_2 indicates that any impurities originating during the exposure to zinc did not produce the line. It should also be pointed out that the line did not appear relatively as strong at K-band frequencies.

In an attempt to study the nature of the adsorption site, the number of spins per gram of magnesium oxide was determined. It was found that MgO II at equilibrium had 3.0×10^{17} CO spins/g MgO. This value may be compared with 6.5×10^{17} atoms Fe/g MgO. In order to establish a minimum number of magnesium-oxygen vacancy pairs which exist on the surface, the degassed MgO was irradiated with 2537Å ultraviolet light to produce paramagnetic S' centers, which are believed to be electrons trapped at the vacancy pairs.[5] When CO was admitted to these samples, the S' center line gradually decreased in amplitude while the CO line increased. Integration of the spectra showed that the number of CO spins after 7 days (approximately half its saturation value) was three times larger than the number of S' radicals.

The number of CO molecules adsorbed on the surface was determined by allowing MgO II to adsorb an equilibrium amount of CO, evacuating the sample at room temperature, and heating it to 800° C while collecting the gas in a large volume. A comparison of the number of molecules of CO desorbed with the number of CO radicals showed that 5% of the CO formed the species with the unpaired electron. Upon exposure to CO, the white MgO became peach colored. The intensity of the color (as determined by visual observation) seemed to grow much more rapidly than the number of spins. Perhaps a large portion of the remaining adsorbed carbon monoxide is associated with this color.

Desorption studies were also carried out by heating a sample in vacuum to progressively higher temperatures for 30-minute periods and observing the decrease in the number of spins. A relative desorption rate was determined by noting the maximum pressure in the dynamic vacuum during the heating. These data, as well as the pressure readings while heating a sample continuously, are presented in Fig. 4. It is apparent that the rate of loss in radicals becomes appreciable near 250° C which coincides with the increased rate of gas desorption.

DISCUSSION OF RESULTS

Analysis of EPR spectra. - The $C^{12}O$ EPR spectra shown in Figs. 1 and 2 are clearly the result of the uniaxial anisotropy of the g-factor.[6] For the $C^{12}O$ spectrum the effect is the result of the anisotropic g-factor rather than the hyperfine splitting, since the spectrum observed at two frequencies leads to the same g-values. It is interesting to note that the calculated curves of Lebedev[6] show that $g_\perp$ is slightly to the high field side of the first major maximum peak when the line width of the individual components is of the same magnitude as the g-factor anisotropy. This point was considered in determining the $g_\perp$-values shown in Table I. The uniaxial anisotropy is certainly consistent with a linear CO molecule. Since both $g_\parallel$ and $g_\perp$ are larger than the free electron g-value of 2.0023, one may also conclude that there are excited states which can combine with the ground state of the adsorbed molecule for a given direction of the magnetic field. These states involve excitation of an inner electron into the half-filled level that contains the magnetic electron.[7]

The hyperfine splitting parameters of Table II give additional information about the unpaired electron. If the unpaired electron is in an s-state, the symmetrical wave function will be a maximum at the nucleus, and considerable isotropic hyperfine splitting will result. The degree of this splitting is measured by the Fermi contact term A_{iso}, which is obtained from the hyperfine spectrum. Should the electron be in the p-state, the interaction with the nucleus is of the dipole-dipole type, and the degree of anisotropic interaction for cylindrical symmetry is given by $A_{\parallel}-A_{iso}$. Pure s-orbital isotropic and p-orbital anisotropic splitting constants have been calculated by Smith and co-workers.[8] The ratio of the s-state contribution in the adsorbed $C^{13}O$ molecule to the pure 2s orbital on a C^{13} nucleus is given by

$$a_s^2 = \frac{A_{iso}}{1110} = \frac{2A_{\perp} + A_{\parallel}}{3(1110)} = 0.0134 \qquad (1)$$

The fraction of p-character is

$$a_p^2 = \frac{A_{\parallel} - A_{iso}}{44.8} = 0.27 \qquad (2)$$

The sum of a_s^2 and a_p^2 gives the fraction of the electron which is associated with the C^{13} nucleus. From this analysis it is apparent that the unpaired electron is about 28% on the carbon[9] and is essentially in a pure p-atomic orbital.

Nature of adsorbed CO radical. - The molecular orbitals of free carbon monoxide are[3] (a) three occupied σ orbitals, corresponding to unshared pairs on the carbon and oxygen atom and a σ bond between these atoms, (b) an occupied doubly degenerate π orbital that contains four electrons, (c) an empty strongly antibonding σ orbital, and (d) a strongly and antibonding π orbital. In forming the metal carbonyl it is postulated that there is a simultaneous transfer of an electron from the σ orbital of the CO molecule to the metal and from the metal to an antibonding π orbital.[3]

This process would result in an unpaired electron in a pure π orbital, and hence the atomic s-character with respect to the carbon atom should be very small.

The EPR evidence indicates that about 5% of the CO molecules are adsorbed in a manner similar to that just described; that is, an electron was transfered from the carbon σ orbital to a surface site while the same site contributed an electron to the antibonding π orbital of the CO. The concept that CO forms a neutral radical rather than a radical anion is supported by the evidence that CO did not react rapidly with the S' defect electron as did the CO_2 molecule to form CO_2^- radicals.[5] In contrast to the reaction of CO with metals, it is felt that the electron source and sink was the magnesium-oxygen ion vacancy pair which existed on the surface. Two facts preclude the iron impurities from being the site for the radical which was observed in this experiment. First, in the case of adsorption on MgO I, the number of spins was nearly equal to the total number of iron ions. The iron would thus have to concentrate almost entirely on the surface, and this is not likely. Equally as important, the iron ion is paramagnetic and would interact strongly with the CO radical. If the dipole-dipole interaction predominated, the line width would be much broader than observed, but if exchange narrowing were significant, the hyperfine lines would not be resolved.[10] The divacancy, on the other hand, offers the required donor-acceptor properties. The region near the positive magnesium ions would be electrophilic while the region around the oxygen ions would have an abundance of electrons. As described in reference 4, the iron as trivalent ions probably provides charge compensation for magnesium vacancies which migrate to the surface upon formation. The minimum number of magnesium-oxygen ion vacancy pairs may be estimated from the number of S' centers which are formed upon irradiation. Only a fraction of the divancies will contain an electron after irradiation, since the ultraviolet light can also remove the electron from the surface trap. The results showed that the concentration of S' centers was about one-sixth the concentration of adsorbed CO radicals at saturation. If less than 20% of the divacancies formed S' centers upon irradiation, then the number of divancies would exceed the number of CO radicals.

CONCLUSIONS

From a study of CO radicals on magnesium oxide with electron paramagnetic resonance, the follow conclusions were drawn:

1. Approximately 5 percent of the carbon monoxide which adsorbs on magnesium oxide forms a radical.

2. The anisotropic g-values and hyperfine constants indicate that this radical is a linear molecule and that the unpaired electron is in a π orbital. These observations are consistent with the bonding in metal carbonyls.

FOOTNOTES

1. R. P. Eischens and W. A. Pliskin, Advan. in Catalysis, 10, 1 (1958).
2. G. Blyholder, J. Phys. Chem., 68, 2772 (1964).
3. L. E. Orgel, "Transition-Metal Chemistry," John Wiley & Sons, Inc., New York, 1950, pp. 135-137.
4. J. H. Lunsford, J. Chem. Phys. (1965).
5. J. H. Lunsford and J. P. Jayne, J. Phys. Chem. (1965).
6. Ya. S. Lebedev, J. Structural Chem. (USSR), 4, 22 (1963).

7. M. C. R. Symons, "Free Radicals in Inorganic Chemistry, " American Chemical Society, Washington, 1962, pp. 76-89.
8. W. V. Smith, P. P. Sorokin, I. L. Gelles, and G. J. Lasher, *Phys. Rev.*, *115*, 1546 (1959).
9. This number may be compared with the results of the simple molecular orbital calculations of Blyholder, [2] which indicate that the unpaired electron is about 33% on the carbon.
10. D. B. Chesnut and W. D. Phillips, *J. Chem. Phys.* *35*, 1002 (1961).

TABLE I. - Table of g-values for CO on MgO.

	$g_{\parallel}$	$g_{\perp}$
$C^{12}O$, X-band	2.0021±0.0003	2.0055±0.0003
$C^{12}O$, K-band	2.0018±0.0003	2.0053±0.0005

TABLE II. - Hyperfine coupling constants for CO on MgO.

	Hyperfine coupling constants, gauss		
53% $C^{13}O$ - 47% $C^{12}O$	$A_{\parallel}$	$A_{\perp}$	A_{iso}
X-band	27.2	8.8	15

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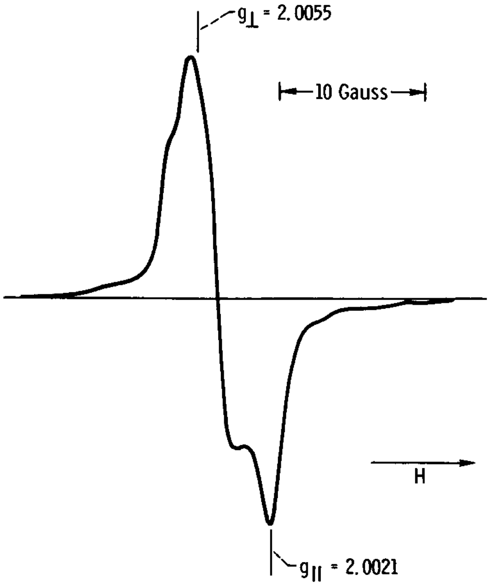

Fig. 1. - EPR derivative spectrum of $C^{12}O$ adsorbed on degassed MgO II. The spectrum is recorded at X-band frequencies.

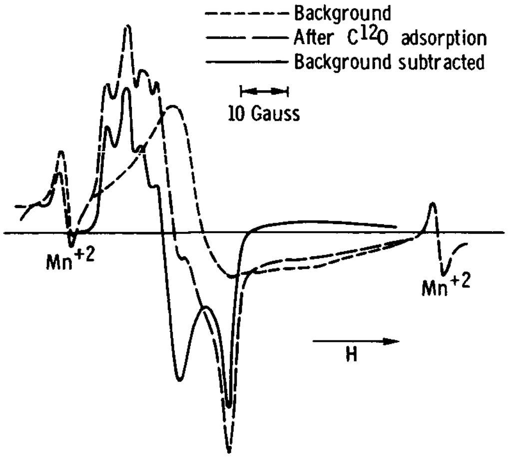

Fig. 2. - EPR derivative spectrum of $C^{12}O$ adsorbed on degassed MgO II. The spectrum is recorded at K-band frequencies.

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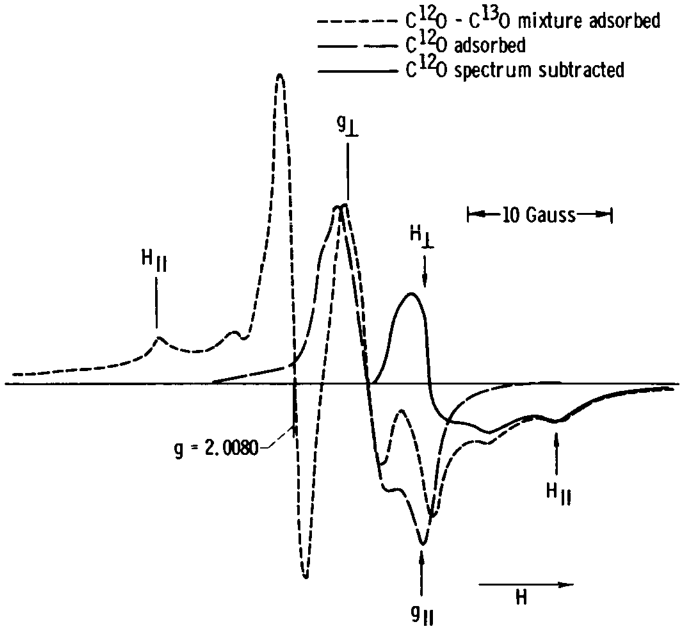

Fig. 3. - EPR derivative spectrum of 53% $C^{13}O$ - 47% $C^{12}O$ mixture at X-band frequencies. The $C^{12}O$ spectrum is subtracted to display the high field hyperfine spectrum.

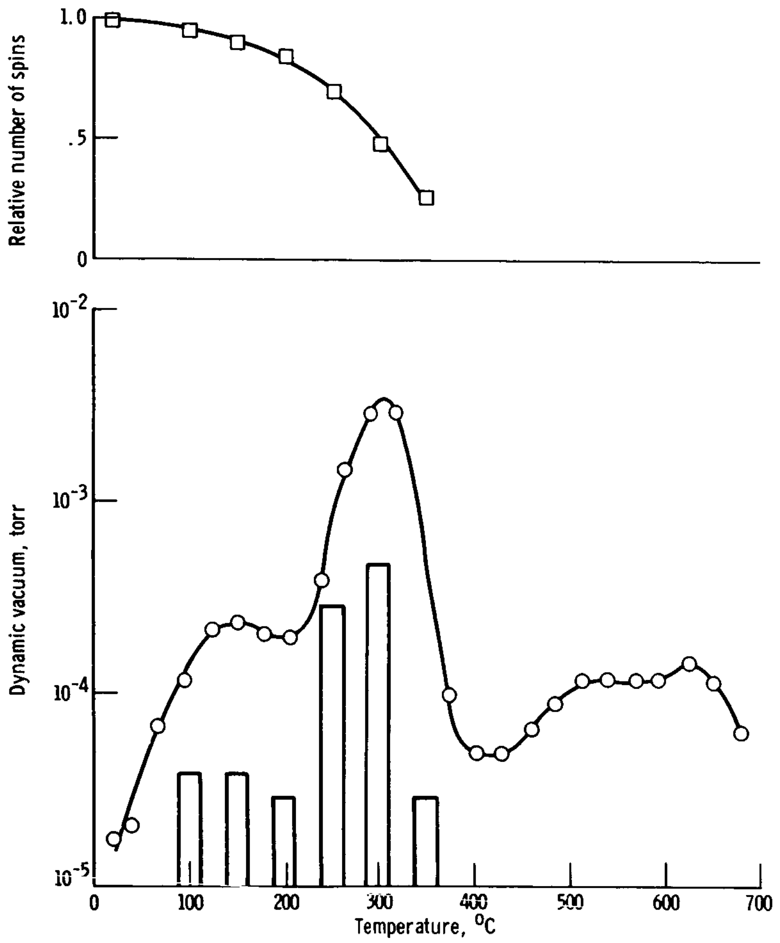

Fig. 4. - Effect of temperature on rate of CO removal from surface of MgO II and on decrease in CO radical concentration: □, relative radical concentration after heating sample 30 minutes to indicated temperature; vertical bar, maximum pressure attained during the heating cycle; ○, pressure during continuous heating of separate sample with CO adsorbed.