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Electron Paramagnetic Resonance of NO Adsorbed on Reduced Chromia–Alumina

M. SHELEF

From the Fuel Sciences Department, Scientific Laboratory, Ford Motor Company, Dearborn, Michigan 48121

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An anisotropic EPR signal has been observed after contact of pre-reduced samples of dilute (0.086–2.31% Cr) chromia-on-alumina with NO. This paramagnetic species is very stable when isolated from ambient conditions but extremely sensitive to oxidation. The width of the signal is independent of temperature or of the Cr concentration in the solid support. The intensity of the signal passes through a maximum as a function of the Cr concentration. The temperature dependence of the signal intensity follows the Curie-Weiss law. The signal is assumed to be associated with the Cr(I) entity resulting from the transfer of the antibonding electron from a chemisorbed NO molecule to a reduced chromous surface site.

The system consisting of NO adsorbed on diluted chromia-on-alumina involves both paramagnetic adsorbate and adsorbent. The EPR of the adsorbent has been thoroughly summarized (*1*) and the EPR of the adsorbate on diamagnetic ionic surfaces has also been studied (*2*). Further, the static susceptibility changes taking place in the adsorption of NO on supported chromia have been measured (*3*). Here, an EPR spectrum resulting from NO adsorbed on diluted and reduced chromia-on-alumina samples is reported.

Samples with Cr content in the range 0.036–2.31% Cr were made by impregnating Kaiser KA-101 alumina pellets with aqueous solutions of $(NH_4)_2Cr_2O_7$ or acidified $Cr(NO_3)_3$. The impurities in the alumina were Fe, 28; Cu, 2.5; and Mn, 1 ppm as determined by atomic absorption spectroscopy. The surface area was 360 m^2/g. The samples were washed with deionized H_2O, dried at 110° and calcined in air at 600° for 8 hr. Uniformly sized spherical pellets were chosen to fit into a quartz tube of 3 mm, i.d., attached as a side arm to a flow reactor. After a desired treatment in the reactor the pellets were transferred into the sidearm without exposure to the air and examined in the EPR spectrometer.

The total amount of NO adsorbed by the samples at room temperature was evaluated by continuous mass-spectrometric monitoring of the outlet composition of a metered He–NO flow over a large bed (~50 g) of the sample pellets, as described in a previous publication (*4*).

Commercial, nonpurified gases were used. The mass-spectroscopically determined impurity levels were as follows: the He carrier gas contained CO, 200; N_2, 600; and O_2, 100 ppm; the CO used in reduction contained 1500 ppm CO_2; the NO contained CO_2, 4000; N_2O, 8200; and NO_2, 3400 ppm.

The spectra were taken on a Varian E-3 spectrometer with a rectangular TE_{102} cavity, operating at 9.5 GHz and equipped with a variable temperature attachment. Recrystallized DPPH was used as the g-value standard. The number of spins per gram was measured by taking the first moment of the derivative signal by the analogue gravimetric method of Burgess (*5*) and comparing the sample moment to that of a standard sample containing a known amount (~1%) of Cu^{2+} ions dispersed in the same Kaiser alumina. The necessary corrections for the density differences were made. The standard was made by grinding $CuSO_4 \cdot 5H_2O$ with the Kaiser alumina. The proportionality of the measured moment to the Cu content was ascertained by examining a series of other impregnated and ground Cu^{2+}-containing samples. The spin density is estimated to be accurate to within ±20%. This uncertainty is mainly due to the difficulty of fixing the signal baseline.

No signal near $g = 2$ was observed from pure alumina treated with NO. After calcination all the samples showed, as expected, a sharp γ-signal [nomenclature of Ref. (*1*)] attributed to Cr^{5+}. Curve A of Fig. 1 gives the intensity of this signal as a function of Cr concentration. The square points taken from Fig. 16, Ref. (*1*), are in agreement with our data. The δ-signal (isolated Cr^{3+}) was almost absent and the β-signal (Cr^{3+} in small clumps) was also faint. Reduction, at 500°, in CO (5%)–He mixtures removes the γ-signal. Passage of the NO–He mixtures over the reduced samples for 15–30 min produces the anisotropic signal of Fig. 2. This signal is typical of spins in axially symmetric environment in polycrystalline solids (*6*). The spectrum of Fig. 2 arises only by contacting the NO with pre-reduced samples. Exposure to air replaces the anisotropic signal by the quasi-symmetrical γ-spectrum. As noted previously by O'Reilly (*7*) the intensity of this room temperature γ-signal is not as strong as that in the calcined samples. Prolonged pumping (>15 min) at room temperature leads to a similar replacement; fast removal of the gas phase leaves the anisotropic spectrum intact. The line width (140 G peak-to-peak) does not change with Cr concentration of the sample in the investigated range or with temperature of the measurement down to 4.2°K. The reciprocal intensity of the signal varies directly as T in the range 113–298°K as shown in Fig. 3. With increase of the NO concentration in the gas mixture in contact with the solid sample, the intensity of the signal shows a definite downward trend as indicated in Table 1. No hyperfine struc-

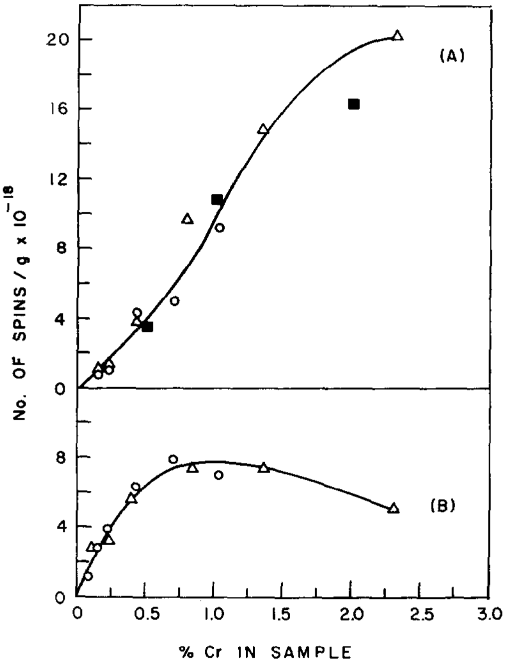

FIG. 1. Change of number of spins per unit weight of sample as a function of Cr content: (A) γ-signal Cr^{5+}, (B) anisotropic signal (at 6.0–7.0% NO in mixture with He). ○, samples impregnated with $(NH_4)_2Cr_2O_7$ solution; △, samples impregnated with $Cr(NO_3)$ solution; ■, from Fig. 16. Ref. (*1*).

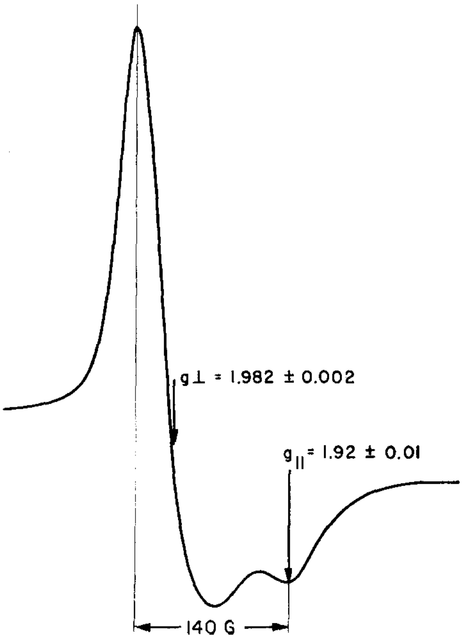

FIG. 2. Derivative of the anisotropic signal.

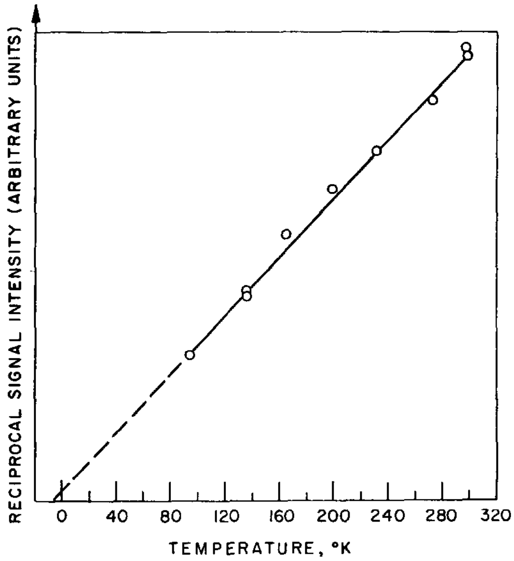

FIG. 3. Temperature dependence of the reciprocal signal intensity in sample with 0.84% Cr.

ture due to ^{14}N could be resolved even at 4.2°K.

Table 2 gives the comparison between the measured number of spins contributing to the anisotropic signal in some of the samples with the total number of adsorbed NO molecules and with the number of Cr atoms in the sample. There is an uncertainty of ±10% in the estimate of the adsorbed amount associated with the reoxidation of the reduced Cr sites by NO. The reoxidation is evidenced by the presence of N_2O and N_2 in the outlet stream. As shown in Table 2, the number of adsorbed molecules and the total number of Cr atoms agree within the limits of error. The number of spins contributing to the anisotropic signal is less than one-tenth of the total adsorbed amount of NO. As shown in Fig. 2, the anisotropic signal is superimposed on a broad signal, presumably that due to Cr^{3+} clumps (β) (*1*) which reduces the accuracy of the baseline determination.

TABLE 1

EFFECT OF NO CONCENTRATION IN GAS PHASE ON THE ANISOTROPIC SIGNAL INTENSITY (0.84% Cr in adsorbent sample)

NO concentration in gas mixture (%)	No. of spins associated with asymmetric signal ($\times 10^{-18}$/g ±20%)
0.54	11.1
0.831	11.5
2.54	12.7
6.19	5.93
6.0–7.0	7.05
22.4	6.25
62.3	3.80

TABLE 2

COMPARISON BETWEEN NUMBER OF Cr ATOMS IN SAMPLE, AMOUNT OF CHEMISORBED NO, AND NUMBER OF SPINS ASSOCIATED WITH ANISOTROPIC SIGNAL

Cr in sample (%)	No. of Cr atoms ($\times 10^{-18}$/g)	No. of NO molecules retained ($\times 10^{-18}$/g)	No. of spins associated with anisotropic signal ($\times 10^{-18}$/g ±20%)
2.31	267	214	4.96
0.84	97	85	7.05
0.70	81	69	7.88

The anisotropic spectrum may be associated with the unpaired electron in the adsorbed NO molecule in which the orbital degeneracy in the $2p\pi^*$ antibonding level has been lifted by the crystal field of the solid surface. In this case the NO could be bonded to the Cr site by a coordinative bond involving a lone pair of 2*s* electrons from the N atom (*8*). Bands in the infrared spectrum of NO chemisorbed on transition metals and their oxides have been attributed to such a mode of surface bonding by Terenin (*9*). One then would expect the anisotropic spectrum to be similar in origin to the spectra ascribed to NO molecules retained on ionic surfaces devoid of transition metal ions. Although the $g_\perp$ and $g_\parallel$ values, and therefore the expected splitting between the $2p\pi^*$ orbitals, are within the range reported by Lunsford (*2b*), there are other reasons which militate against such an interpretation. These are: (i) the experimental evidence from static susceptibility studies that the chemisorption of NO on supported Cr is associated with the transfer of the antibonding electron to the transition metal atom which serves as the chemisorption site (3); (ii) scanty evidence (*8*) for the formation of nitrosyl complexes in which the coordinative type of bonding prevails; and (iii) the total absence of hyperfine structure due to ^{14}N.

The following interpretation of the anisotropic signal is offered here. After reduction the surface Cr ions are in an average oxidation state between Cr^{2+} and Cr^{3+}, a substantial number being obviously in the Cr^{2+} state (*5, 10, 11*). Passage of the He–NO mixture results in: (i) partial reoxidation of the Cr on the surface; (ii) chemisorption on all Cr sites as noted in Table 2. It is plausible to assume that the NO_2 and O_2 impurities originally present in the gas mixture are in part responsible for the reoxidation and that the Cr^{2+} surface ions are the most susceptible to it. We propose that the anisotropic signal comes from the relatively small amount of Cr^{2+} sites on which the NO has been chemisorbed without reoxidation. If this chemisorption is associated with a transfer of the antibonding electron to the chromous ion, the resulting entity is analogous to that observed by EPR in Cr(I) complexes of NO, i.e., to a $^5dNO^+$ structure (*12*). The signal cannot be attributed to a higher oxidation state of the chromium ion because the spectra coming from well explored reduced and oxidized specimens containing Cr surface states from Cr(II) to Cr(VI) are quite different (*1*). The immediate disappearance of the anisotropic signal on contact with air, or on prolonged pumping and its decrease with the increased NO content in the gas phase, can all be rationalized by the extreme sensitivity of the Cr(I) to oxidation.

It is worth noting the closeness of the *g*-values observed by Bernal *et al.* (*12*) in rigid Cr(I) nitrosyl complexes to those of Fig. 2. The axial symmetry, according to these authors, is indicative of a linear M–N–O group as was predicted by Gray *et al.* for a $^5dNO^+$ structure (*13*). There can be several explanations for the absence of the hyperfine structure due to ^{14}N, the most plausible being a very low unpaired spin density on the NO ligand. Another cause may be the broadening out of the hyperfine structure by interaction with the neighboring $^{27}Al(I = 5/2)$ nuclei as suggested by Lunsford (*2c*).

Extrapolation of the least squares line of Fig. 3 yields a Weiss constant value of −6.5°K. This deviation from the Curie behavior could be due to the experimental error in the measurement of the temperature or to the scatter of the experimental points and the extrapolation. A low value of the Weiss constant is taken as an evidence of the absence of exchange interactions at the concentration of 0.84% Cr, i.e., that the ions contributing to the signal are magnetically well isolated.

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