Sorption and Magnetic Susceptibility Studies on Nitric Oxide-Hydrated Chromic Oxide Systems on Silica Gel

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The chemisorption of NO on diluted Cr_2O_3 complex supported on silica gel gives proof for a pairing of d-electrons in the chromium complex with the single electron in NO. The Cr atoms seem magnetically isolated. The reason for the unusually high magnetic moments of the physically adsorbed NO is discussed. These high moments are previously found for NO on pure silica gel, alumina gel, and in clathrate compounds. The supported Cr_2O_3 complex does not affect the amount nor the state of the physically adsorbed NO.

Previous work on the adsorption of NO on silica gel [1] and on alumina gel [2] at low temperatures revealed a higher magnetic moment on the adsorbed NO than in the gas phase at the same temperature. At 193° and 181°K the effective Bohr magneton number of the adsorbed gas up to nearly monolayer coverage was approximately 2 instead of 1.735 and 1.717, respectively, as reported theoretically [3] and experimentally [4] for gaseous NO. The point on the isotherms beyond which adsorbed NO had the same magnetic moment as in the gas phase turned out to be in the order of magnitude of 10^{14} molecules NO/cm^2, or approximately monolayer coverage.

The experiments on alumina gel were complicated by a chemisorption of NO, the rate of which was so small, however, that the amount physically adsorbed could easily be calculated from the rate curves and the magnetic data. The experiments revealed the physically adsorbed NO behaving in the same manner on this adsorbent as on silica gel, *i.e.* having a Bohr magneton number near 2 at lower temperatures. Qualitatively Cooke and Duffus [5] found the same effect of NO in a clathrate compound.

The system reported in this paper, nitric oxide adsorption on diluted chromium oxides supported by silica gel, was interesting because NO was rapidly chemisorbed on the chromium complex with comparatively great effect on the overall magnetic susceptibility. The spin quantum number of a chrome unit was calculated to decrease with 1/2 during this chemisorption, indicating pairing of one electron. The physically adsorbed NO behaved in the same manner as on pure silica gel.

No attempt was made in this study to examine the magnetic behaviour of the chromium complex as a function of dilution. Attempt was made, however, by magnetic analysis to determine the state of the chromium complex with and without chemisorbed NO, and to determine the influence of chromium oxides on the adsorptive capacity of silica gel. Emmett and Cives [6] reported that chemisorption of hydrogen on chromium gel in no way affected the physical adsorption of H_2 and N_2. Similar data for NO is not available.

Turkewich [7] could find no marked effect on chromium oxide gel when chemisorbing H_2. As shown in this paper the chemisorption of NO on silica gel supported chromium oxide has indeed a great effect on the susceptibility of the system, indicating pairing of unpaired electrons in the chromium complex.

EXPERIMENTAL

The equipment and technique used is essentially the same as reported elsewhere.[1,2] The equipment consisted of a vacuum, silica helical thermo balance placed in the field of an accurately regulated electro magnet with a field strength of about 9000 Gauss, and with a force constant $H \, dH/ds = 5.3 - 5.4 \times 10^6$ slightly dependent on temperature as previously reported.

The sample was made in accordance with a description of Flid and Kagan.[8] The silica gel of the same grade and purity as reported previously [1] was carefully dried and allowed to absorb from a solution of CrO_3 in distilled water for 20 min. It was filtered, washed briefly and dried at 120°C. It was reduced to Cr_2O_3 by heating to 480°C in a constant stream of hydrogen for 9 h. The colour then changed from brown-yellow to green. The BET-surface was 520 m^2/g, slightly less than that for the original silica gel. The analysis on the chromium content was made by pulverizing part of the sample, oxidizing with HNO_3 and a small amount of potassium chlorate, decanting and the residue treated with NaOH. Both solutions were mixed, diluted with 0.5 N H_2SO_4 and electrolyzed boiling with 2 Pt-net cylinders as electrodes. The cathode was weighed until constant weight.

The analysis showed 3.20 % Cr_2O_3, amounting to 0.208 mmole Cr_2O_3/g silica gel.

RESULTS

The results of the adsorption measurements are shown on Fig. 1 for 183° and 213°K and on Fig. 2 for 243° and 273°K (unbroken line, left scale). The
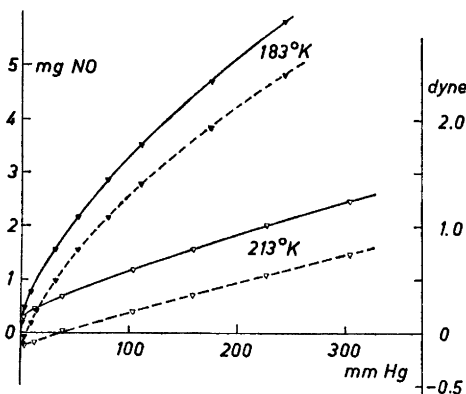

Fig. 1. NO adsorption on silica gel supported chrome oxide at 183° and 213°K. Adsorption is given by unbroken line and left scale, while magnetic measurements are given by broken line and right scale.
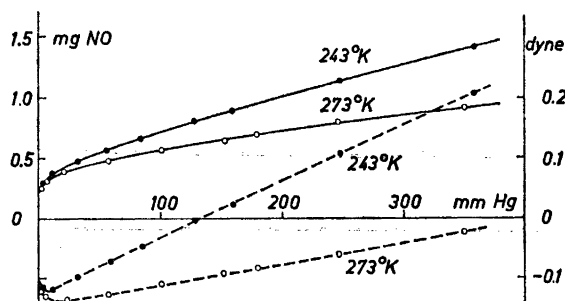
Fig. 2. NO adsorption on silica gel supported chrome oxide at 243° and 273°K. Adsorption is given by unbroken line and left scale, while magnetic measurements are given by broken line and right scale.

isotherms, even at 273°K are very steep at low pressures contrary to those found on pure silica gel,[1] suggesting that a chemisorption with a high heat of adsorption is taking place. This is confirmed by the magnetic measurements shown on the same figures (broken line, right scale), indicating that the paramagnetism of the supported chromium complex decreased at first, before the overall susceptibility of the sample increased due to the physically adsorbed NO.

When plotting the force as a function of the adsorbed amount of NO, as is done on Fig. 3 for 183°K and on Fig. 4 for 213°K, we see that the susceptibility increases in a way that a) suggests that further adsorption only involves physical adsorption, and b) that the physically adsorbed NO behaves in the same manner as on pure silica gel, i.e. with a higher magnetic moment than that for the gas phase at the same temperatures. The figures for 273°K, although not shown graphically, reveals that at this temperature the magnetic moment
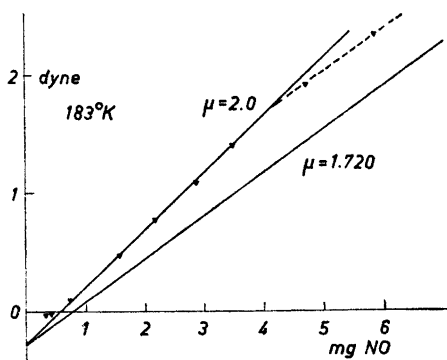

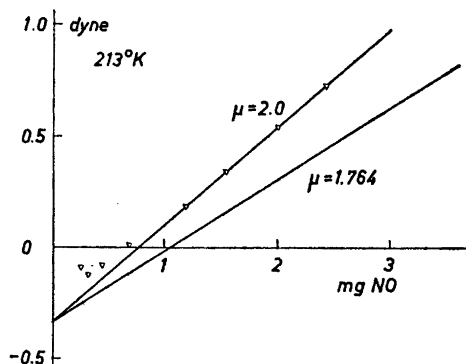Fig. 3. Force in the inhomogeneous magnetic field as a function of adsorbed NO. 183°K.

Fig. 4. Force in the inhomogeneous magnetic field as a function of adsorbed NO. 213°K.
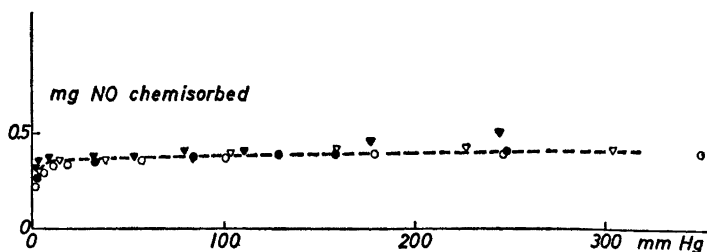
Fig. 5. Amount NO chemisorbed on the samples at different temperatures as a function of pressure. Symbols: ▼ 183°K, ▽ 213°K, ● 243°K and ○ 273°K.

of the adsorbed NO is the same as that for the gas phase at the same temperature, as shown for pure silica gel. The figures for 243°K show a slight deviation towards higher magnetic moments at low coverages, but the accuracy was here low due to the chemisorption of NO on the chromium complex.

The magnetic data used under the reasonable assumption that the physically adsorbed NO possesses the same properties at low coverages as it does at a concentration where they can be read from data like those on Figs. 3 and 4 makes it possible to calculate the amount chemisorbed on the Cr_2O_3 complex. This is given on Fig. 5, showing a strong chemisorption. The trends of the points are right, but the accuracy does not warrant any drawing of isotherms which can be used for the calculation of the heat of chemisorption.

The physically adsorbed NO as a function of pressures is given in Fig. 6, and is comparable in size to the values found on pure silica gel.[1] The heat of physical adsorption calculated from these curves by the Clausius-Clapeyron equation is of the order of magnitude of 4 kcal as found on pure silica gel.

The data also makes it possible to calculate the decrease in the susceptibility of the chromium complex as a function of NO adsorbed, evidently under pairing of electrons. As seen from Fig. 7 the decrease is proportional to the amount adsorbed, as would be expected for a magnetically diluted substance.
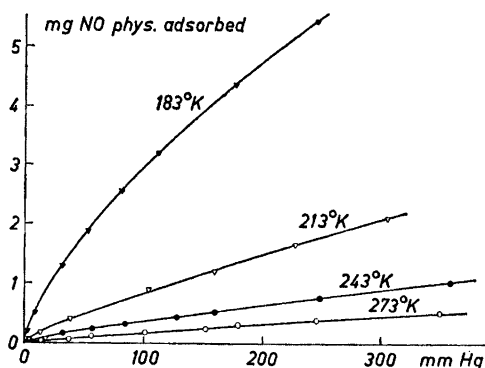

Fig. 6. Amount NO physically adsorbed on the sample at different temperatures as a function of pressure.
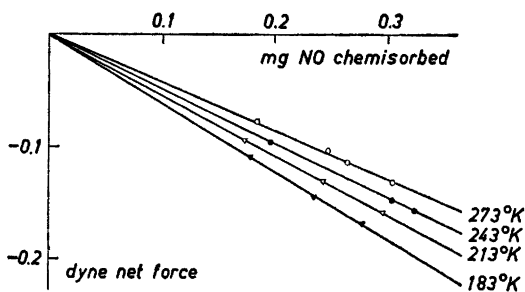
Fig. 7. Change in net force as a function of chemisorbed NO at different temperatures.

DISCUSSION

The Cr-complex and chemisorption of NO. The adsorbed chromium compound is very diluted. From the mentioned analytical data and assuming that 1 NO reacts with 1 $Cr_2O_3 \cdot nH_2O$ unit, we find that the oxide covers about 2.7 m^2/g silica gel or about 0.5 % of the surface. The middle thickness is 4.68 molecule units (calculated as $Cr_2O_3 \cdot nH_2O$). It is therefore to be expected that the chromium compound will not affect the physical adsorption on the silica gel, as also is evident from the adsorption data.

The Cr_2O_3 is obviously in a hydrated form, as we see from Fig. 8, where the mole susceptibility is compared to other known chromium oxide compounds. It reveals that the temperature dependence is different from pure Cr_2O_3 which is almost independent of temperature. The close similarity to the curves for the hydrated forms is ample proof for a hydrated state when supported on silica gel. One must not overlook the possibility that extreme dilution may influence the susceptibility as found for Pd [9] and other substances,[10,11] yet this is not to be expected here in opposition to metallic states where the exchange effects are several orders of magnitude higher, and where the dispersion highly influences the magnetic character as on Pd.[9]

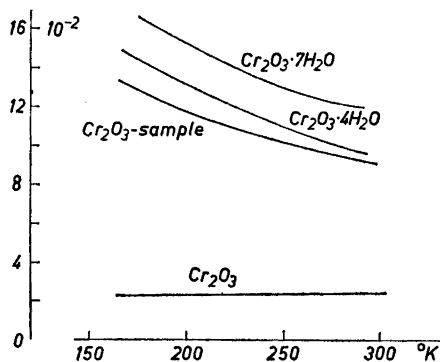One interesting point is whether the Cr-atoms are magnetically coupled

Fig. 8. Molar magnetic susceptibility of sample compared with other forms of Cr_2O_3-complexes.

Table 1. Magnetic moments of the chrome-complex before and after adsorption of
1 NO/Cr$_2$ and 1 NO/Cr unit, respectively.

$T°K$	$\chi_{Cr_2}{}^a$	μ_{Cr_2} eff	$\chi_{Cr}{}^a$	μ_{Cr} eff	$\dfrac{NO/Cr_2}{\mu_{Cr_2}\text{ eff}}$	ΔS_2	$\dfrac{NO/Cr}{\mu_{Cr}\text{ eff}}$	ΔS_1
183	12.38×10^{-2}	4.3	6.19×10^{-2}	3.05	3.63	-0.32	2.04	-0.47
213	11.19×10^{-2}	4.4	5.60×10^{-2}	3.13	3.76	-0.31	2.10	-0.48
243	10.28×10^{-2}	4.5	5.14×10^{-2}	3.20	3.89	-0.31	2.20	-0.47
273	9.49×10^{-2}	4.6	4.75×10^{-2}	3.26	3.99	-0.31	2.30	-0.45

^{a} Molar susceptibilities.

in, say, Cr$_2$ units or whether the exchange effects are so small that each Cr unit is magnetically isolated. Table 1 gives the μ_{eff} calculated before and after adsorption of NO. Assuming the susceptibilities may be represented by a spin-only function, as has been shown by several authors for Cr^{3+} (see Ref. 3, p. 285 ff.), we see from Table 1 that the spin quantum number S decreases with approximately 1/2 for the case when the single Cr atom is treated as the magnetic unit. This confirms the pairing of an unpaired d-electron in the Cr unit with the single electron in NO. The slight deviations from 1/2 may point to a certain exchange effect, but the values are probably within the experimental errors of the system. With the lacking exchange effects, it is also highly probable that no surface states are present, at least surface states involving change in the d-structure.

Physical adsorption of NO. The effective Bohr magneton number of approximately 2 found for adsorbed NO at 183° and 213°K, compared to 1.720 and 1.764, respectively, found for gaseous NO, is in accordance with the data on pure silica gel [1] and on alumina.[2]

The NO molecule has a $^2\Pi$ structure with a doublet width of only 352 cal/mole or in the order of magnitude of kT which is the reason for the deviation from the Curie law. Taking into account the spin quantum number, van Vlecks theory [3] leads to the formula for the effective Bohr magneton number:

$$\mu_{eff} = 2 \sqrt{\frac{1-e^{-x} + x \cdot e\, x^{-1}}{x \cdot e^{-x} + x}} \qquad (1)$$

where $x = h\Delta\nu/kT$ with $h\Delta\nu$ the doublet width. The theory of course assymptotically leads to the limiting cases:

a) at low temperature where $h\Delta\nu >> kT$, where the effective magneton number equals $(\Lambda + 2\Sigma)$, where Λ, the orbital component is 1 for this $^2\Pi_{1/2}$ state, and the spin quantum number $\Sigma = -1/2$ as the lowest state, giving $\mu_{eff} = 0$ for the $^2\Pi_{1/2}$ state.

b) at high temperatures where $h\Delta\nu << kT$ where the magneton number is given by

$$\sqrt{(4S(S + 1) + \Lambda^2}} \qquad (2)$$

where $S = 1/2$ and $\Lambda = 1$. (It is proportional to Λ^2 and not to $L(L + 1)$ as is the case with atoms because the multiple splitting of the orbital moment is very large in molecules.) This leads to an effective Bohr magneton number of 2 for the $^2\Pi_{s/s}$ state.

In between these extreme values the effective Bohr magneton number can be calculated by van Vlecks formula in excellent agreement with experimental data over the whole temperature range.

The effective Bohr magneton number near 2 measured in our case at lower temperatures must obviously be due to strong interactions with the surface. These interactions are obviously highly dependent on the distance from the surface as they disappear at higher surface coverages or at higher temperatures, both reasons for a larger equilibrium distance from the surface.

Examining formula (1) we see that when the doublet width $h\Delta\nu$, which in turn is an explicit expression of the coupling between the spin and orbital of the single electron in NO, diminishes, the effective Bohr magneton number equals 2, as the expression under the square root sign goes towards 1. In fact a decrease of $h\Delta\nu$ to about $1/10$ (or $30-40$ cal/mole) will make the effective Bohr magneton number about 1.98, or the same as found on silica gel, and within the experimental error for the number 2 used in this publication.

This effect on the coupling energy has also been found qualitatively in other systems, for instance in the measuring of the magnetic susceptibility of NO enclosed in a clathrate compound,[5] where the data at low temperatures fitted a curve calculated with a doublet width of about 50 % of that found in gaseous NO, increasing gradually to the doublet width found for gaseous NO at a temperature around 300°K.

The high momenta measured could of course in principle be assigned to other effects than a decrease in coupling energy, say a higher degree of order in the field direction of the sample. This, however, is unlikely as the directions in the sample are quite haphazard, and that orientation like that in no way principally would lead to a magneton number of 2.

The explanation of the decrease of the energy of coupling will only be speculative at this stage. How an external field will affect the coupling constant must be the basis for perturbation calculations.

At least in principle one may assume that a field from the surface will distort the orbital in a way that the coupling energy will diminish. This would be interesting as it could form the foundation for a chemisorption model, as we have seen on alumina gel. However, what influence such a distortion would have on the orbital quantum number which in a high degree determines the Bohr magneton number as seen from (2) is difficult to say. The field used as a model must not quench the orbital angular momentum.

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