

The Adsorption of Nitric Oxide on Iron Oxides

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Adsorption isotherms and rates were measured for NO chemisorption on supported and unsupported samples of Fe_2O_3 and Fe_3O_4 in the 26–150°C temperature range. The adsorption behavior is well described by Freundlich isotherms in the pressure range from 1 to 200 Torr. Monolayer coverage is attained at 500 Torr for the reduced samples and at 25 000 (by extrapolation) on the oxidized samples.

Kinetic measurements were evaluated using the Elovich equation. These plots were monotonic in the case of supported Fe_2O_3 and showed a sharp discontinuity in the case of supported Fe_3O_4 at $\theta = 0.5$.

A close parallelism is noted with previously studied chemisorption behavior on reduced and oxidized supported chromium oxide.

INTRODUCTION

The present work is a continuation of our gravimetric studies of NO chemisorption on the surfaces of transition metal oxides (1) which may serve as catalysts in the reduction of nitric oxide. Supported iron oxide shows remarkable activity in the reduction of NO by carbon monoxide (2). Iron was shown to chemisorb NO readily in different oxidation states (3–5), and also to form a wide spectrum of inorganic complexes with NO (6). Since the catalytic reduction of NO is known to be strongly affected by the presence of oxygen it is of interest to investigate the chemisorption process in various states of oxidation of the iron oxide.

To characterize the chemisorption properties of the iron oxides, supported samples of various surface iron concentrations and also of pure iron oxide were used. A comparison is made also between the previously explored chemisorption on chromium oxide and the present results.

EXPERIMENTAL METHODS

A. Adsorbents

The carrier for the samples of supported iron oxide was the same as that which had been used in earlier experiments (1) consisting of 95% alumina and 5% silica (sup-

plied by the American Cyanamid Co.). The support was impregnated with an aqueous solution of ferric nitrate and calcined at 600°C for 8 hr. The supported samples had to be kept in a vacuum for about 1 week until reproducible measurements could be obtained. Most of the adsorption studies were carried out on sample S1, containing 8.15 wt % of iron. Sample S1 lost 3% of its weight during the pretreatment. Two other supported samples of iron oxide, designated S2 and S3, contained 0.85 and 0.15 wt % of iron, respectively. Unsupported Fe_2O_3 (α phase according to x-ray analysis) and Cr_2O_3 , used for comparison, were "specpure" specimens supplied by Matthey, Johnson and Company.

The BET surfaces were determined gravimetrically by adsorption of argon at the temperature of liquid nitrogen, using 16.9 \AA^2 as the area occupied by an Ar atom (7) and $p_0 = 202.9$ Torr as saturation pressure (8). In case of the relatively small surface area of unsupported iron oxide, the BET surface was also measured volumetrically by the adsorption of krypton at the temperature of liquid nitrogen. Both methods gave results agreeing within better than 2%.

The supported samples were oxidized under 10 Torr of oxygen at 450°C. Reduction was carried out at the same tempera-

ture by a gas mixture consisting of 20 mole % CO and 80 mole % CO₂. The gas mixture was prepared by subliming purified CO₂ from a small trap into a large storage vessel containing CO at a known pressure. A pressure of 100 Torr of this reducing mixture was kept in the sample chamber for 1 hr; after evacuation it was replaced by 200 Torr of the same mixture which remained in contact with the sample until the reduction was completed. Reduction of Fe₂O₃ under those conditions results in Fe₃O₄ (9). The samples were evacuated after completion of the oxidation and reduction processes for about 1 hr before they were cooled to the desired temperature of adsorption. Weight constancy was always established before admission of the adsorbate.

Oxidation and reduction of the unsupported samples were carried out at 350°C to minimize surface shrinkage.

While the oxidation was completed within a few hours, the reduction process was found to be much slower and proceeded for at least 10 hr.

A shrinkage of the BET surface which had been observed previously for supported chromia exposed to NO (1) was also found for supported iron oxide. Sample S1 had a total surface of 198.9 m²/g at the beginning of the adsorption studies. After completion of the measurements only 154.4 m²/g were measured. A concomitant shrinkage of the iron oxide surface was indicated by a decrease of the NO adsorption. The amount of NO which was adsorbed under specific conditions was noticeably smaller after the sample had undergone several oxidation-reduction cycles.

The surface of the unsupported iron oxide decreased only by 3% during the relatively short duration of the adsorption experiments. The original surface was 12.40 ± 0.20 m²/g of Fe₂O₃. The BET area per sample did not change when Fe₂O₃ was reduced to Fe₃O₄.

The BET area of pure α -Cr₂O₃ was 4.92 m²/g.

It was observed for all samples of iron oxide that the reduction of Fe₂O₃ to Fe₃O₄ was accompanied by a larger weight decrease than required by the stoichiometry

of the reaction. This extra amount of oxygen is assumed to be picked up by the Fe₂O₃ surface and will be discussed later.

B. Adsorbate

In the previous communication (1) we have not given the complete purification procedure therefore its detailed description is given here.

The purification of nitric oxide was rather troublesome and time consuming. Even so, the purified product still contained small amounts of nitrogen (0.2% or less) and traces of nitrous oxide (N₂O). Analysis by mass spectrometer did not detect any contamination by NO₂ or N₂O₃ in the final product.

The best result for NO purification was obtained by the following procedure. Nitric oxide from a commercial gas tank was first frozen in a trap at the temperature of liquid nitrogen and then pumped on for 0.5 hr. The solid NO was warmed slowly until the liquid phase had formed, releasing considerable amounts of dissolved nitrogen. The trap was cooled again in liquid nitrogen and evacuated. This process was repeated five times. When warming up the trap for the sixth time, the first fraction of about 10% was discarded, while expanding the middle fraction into a storage bulb. The trap was placed into a Dry Ice-acetone bath during the warming process. A remainder of 20% of the liquid was also rejected. This fractionation was repeated at least six times. The portion of NO which was retained as end product was only about 10% of the original amount. The liquid appeared straw-green before the end of the purification process as has been reported by Nightingale *et al.* (10). However, our final product was bluish in the liquid state, resembling liquid oxygen. A slightly grayish tint of the solid, which had been observed previously (1) was caused by mercury in the purification trap. Solid NO in the mercury free parts of the apparatus was white.

C. Execution of Measurements

The particulars of the electrobalance system and the associated equipment have been described earlier (1). Adsorption isotherms were measured on sample S1 at 26.

90, and 150°C for oxidized and reduced surfaces. Systematic errors caused by aging of the catalyst were limited by alternating isotherms for oxidized and reduced surfaces and measuring consecutive isotherms at different temperatures. The repetition of adsorption points under specific conditions (e.g., measuring the NO uptake at room temperature and 170 Torr) after the completion of an isotherm was used as a basis to correct for surface shrinkage. A correction was applied by multiplying the adsorbed amount at each point of the isotherm by the factor which was derived correspondingly, assuming that the surface remained constant during each series. This correction factor did not exceed 1.15. The correction is smaller than the total shrinkage of BET area mentioned previously. This may be due to the fact that the total shrinkage of the BET area was measured after additional drastic treatments such as an attempt at a complete reduction of the iron oxide by H₂. The criterion for adsorption equilibrium on the iron oxide surfaces was the same which had been used for the adsorption of NO on chromia (1). Adsorption was continued for 6 to 24 hr until the amount adsorbed per hour was less than 0.2% of the quantity already adsorbed. The total amount of adsorbed NO was corrected for the small amount which was adsorbed on the alumina-silica surface. This quantity was determined in a separate experiment. Consistency of the results was

checked by repeating one or more points of each isotherm after the sample had been subjected to at least one oxidation-reduction cycle.

Adsorption rates of NO on sample S1 were measured at 26, 90, and 150°C and a constant pressure of approximately 3 Torr. These measurements were executed for the oxidized and for the reduced surface and were repeated at least once.

EXPERIMENTAL RESULTS AND DISCUSSION

A. Adsorption Isotherms

The unit of adsorption is "millimoles of NO per gram of catalyst in its initial state," 1 g of catalyst corresponding to a BET surface area of 198.9 m²/g. Obviously, only a part of the total exposed surface is iron oxide. Adjustment for surface shrinkage is taken into account as described above. The adsorption isotherms for sample S1 are shown in Fig. 1 for Fe₂O₃ (filled symbols) and Fe₃O₄ (open symbols). The data conform well to Freundlich isotherms in the covered pressure range from 2 to 200 Torr, as shown by a linear relationship between the logarithmic coordinates of the amount adsorbed, q , and the pressure p . The Freundlich isotherm is defined by

$$q = cp^{1/n}, \quad (1)$$

where the coefficients n and c are functions of the temperature, and these can be expressed by the amount q_m which is ad-

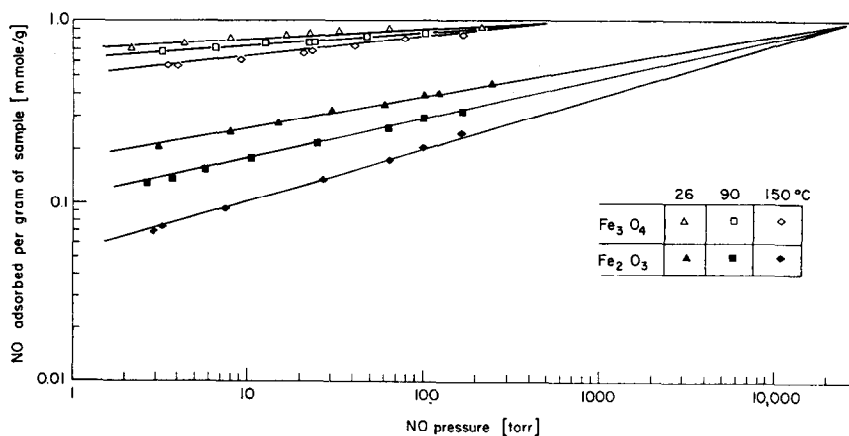


FIG. 1. Adsorption isotherms for NO on supported iron oxide: Δ , \square , \diamond : Fe₃O₄; \blacktriangle , \blacksquare , \blacklozenge : Fe₂O₃.

sorbed at monolayer coverage ($\theta = 1$), the pressure $p_m = 1/a_0$ required for formation of a monolayer, and H_m which is a measure for the heat of adsorption (1, 11). These relationships are

$$n = H_m/RT, \quad (2)$$

where T is the absolute temperature, and

$$\log c = \log q_m + (1/n) \log a_0. \quad (3)$$

The points of intersection for both sets of isotherms show that the amount of NO required for monolayer coverage is identical for Fe_2O_3 and Fe_3O_4 , i.e., $q_m = 0.96$ mmoles/g. However, the pressure which is necessary to achieve monolayer coverage is much higher for Fe_2O_3 ($p_m = 25\,000$ Torr) than for Fe_3O_4 ($p_m = 500$ Torr), demonstrating that the affinity for NO at a given pressure is much higher for the reduced surface than for the oxidized surface.

The significant parameters of the Freundlich isotherms are given in Table 1. Both coefficients c and n decrease with temperature which is the usually observed behavior (11). The values for n in case of Fe_2O_3 are close to those which have been reported for oxidized chromia. From Eq. (2), n can be considered as a measure of the affinity of the surface toward NO adsorption. One derivation of the Freundlich isotherm, based on statistical thermodynamics, requires that the product nT should be constant, but it is experimentally quite frequently found that this product decreases with temperature, which is also the case for the data given for Fe_2O_3 and Fe_3O_4 in Table 1.

Assuming a logarithmic decline of the

TABLE 1
COEFFICIENTS OF FREUNDLICH ISOTHERMS

	$T_c(^{\circ}\text{C})$	n	$H_m (= nRT)$ (kcal/mole)	c (mmole/ g)
Oxidized surface (Fe_2O_3)	26	6.01	3.57	0.178
	90	4.67	3.37	0.110
	150	3.51	2.95	0.053
Reduced surface (Fe_3O_4)	26	20.02	11.89	0.704
	90	14.91	10.75	0.632
	150	10.78	9.06	0.539

heat of chemisorption with coverage, $H_o = -H_m \ln \theta$ (11), the proportionality constant H_m is interpreted as the heat of adsorption at a coverage $\theta = 0.37$. The averaged value of H_m for the oxidized surface in the range from 26 to 150°C is 3.3 kcal/mole. The corresponding value for the reduced surface is much higher: 10.5 kcal/mole.

The isosteric heat of adsorption can also be calculated from the family of isotherms with the aid of the Clausius-Clapeyron equation. The value which is thus derived for the oxidized surface, corresponding to H_m ($\theta = 0.37$), is 5.5 kcal/mole for the oxidized iron oxide surface. The result is in numerical agreement with the heat of adsorption calculated for oxidized chromia at the same coverage (1). The reduced surface yields in the same manner 14.7 kcal/mole. This last result is obtained by employing a considerable extrapolation.

B. Adsorption Rates

Adsorption rates were evaluated by plotting them in accordance with the Elovich equation,

$$dq/dt = a \exp(-\alpha q), \quad (4)$$

with q in mmoles/g, t in seconds, or its integrated form,

$$q = \frac{2.3}{\alpha} \log \frac{t}{t_0}, \quad (5)$$

assuming $t_0 = \frac{1}{a\alpha} \ll t$.

The Elovich plots for Fe_2O_3 and Fe_3O_4 are qualitatively similar to those obtained for oxidized and reduced chromia (1). The NO adsorption on reduced surfaces is characterized by a fast uptake of NO at low coverages which is followed by a much slower process. The result is an Elovich plot consisting of two linear segments with a distinct break between them, as shown in Figs. 2 and 3. The equivalence of plotting the data according to Eqs. (4) and (5) is evident from a comparison of both graphs. The break occurred at all temperatures at a coverage of 0.47 ± 0.04 mmoles of NO/g, which corresponds to $\theta \sim 0.50$. In contrast, adsorption on oxidized surfaces yields an

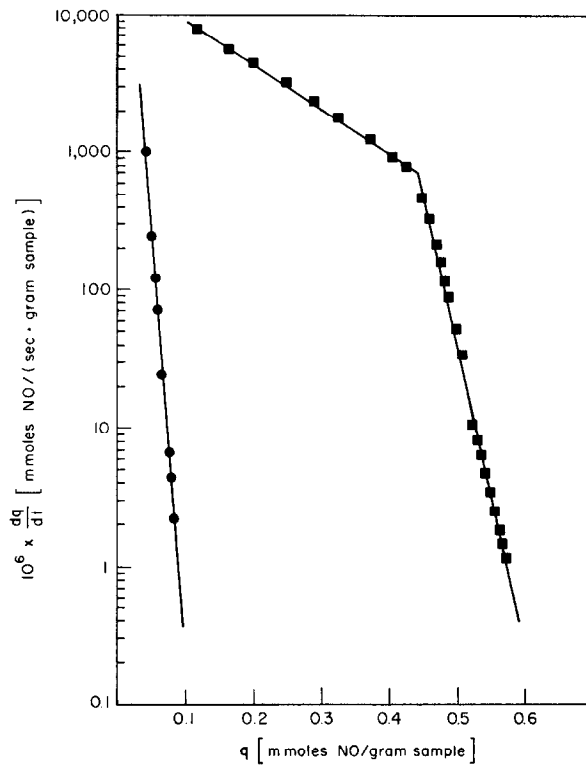


FIG. 2. Elovich plots for NO adsorption on supported iron oxide at 90°C and 3.5 Torr: \blacksquare : Fe_3O_4 ; \bullet : Fe_2O_3 .

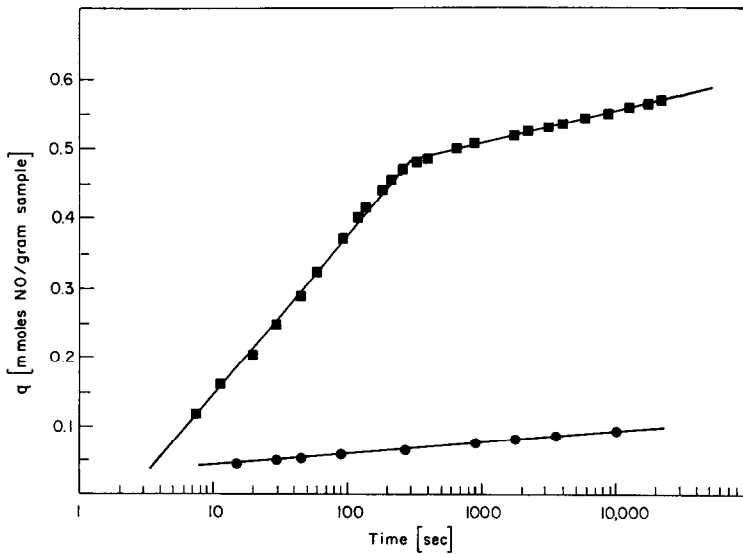


FIG. 3. Elovich plots for NO adsorption on supported iron oxide, integrated form at 90°C and 3.5 Torr: \blacksquare : Fe_3O_4 ; \bullet : Fe_2O_3 .

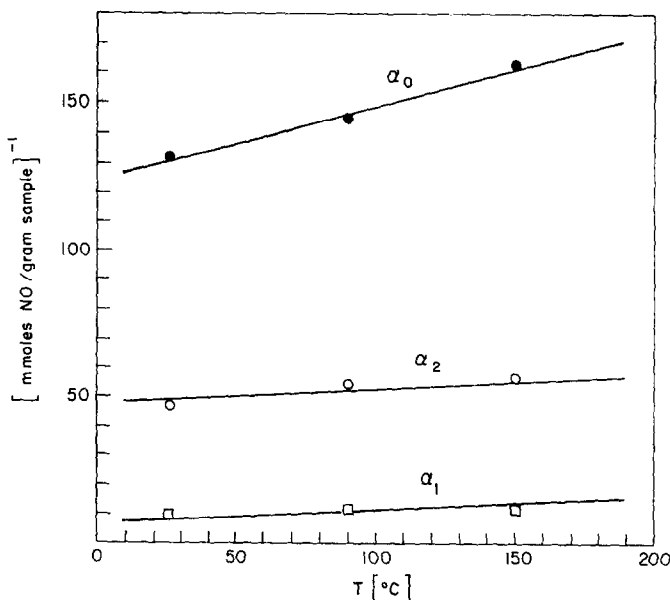


FIG. 4. Temperature dependence of α from Elovich plots: α_0 (●): Fe_2O_3 ; α_1 (□): Fe_3O_4 (first line segment); α_2 (○): Fe_3O_4 (second line segment).

Elovich plot which consists of a single straight line.

The adsorption rates depend primarily on the exponential factor α , while the pre-exponential factor a is of less importance. The coefficients α_1 and α_2 given in Fig. 4 describe the first and second linear segment of the Elovich plots for supported Fe_3O_4 ; α_0 follows correspondingly for Fe_2O_3 . An increase of α is equivalent to a decrease of the adsorption rate. A comparison of α_0 and α_1 confirms again the difference between the adsorption rates on oxidized and reduced iron oxide. For example, the ratio of these rates at a coverage $\theta = 0.1$ and room temperature is 2×10^5 , and this ratio increases by a factor of 10 upon raising the temperature to 150°C .

C. Irreversibility of NO Adsorption

In the previous work with chromia (1) the chemisorption of NO on the oxidized surface was completely reversible, while on the reduced surface it was irreversible to a small degree. In the case of the iron oxides the degree of irreversibility is higher. Thus, the desorption of NO both from the reduced and oxidized surfaces was slow and incomplete. For example, after contacting

the reduced surface with NO at 215 Torr and 150° , 81 wt % of the adsorbed amount remained on the surface after 3 hr of pumping, 57% upon raising the temperature to 215° for 2 hr, and 35%, corresponding to 10.5 mg/g, was retained at 288°C . A corresponding desorption from an oxidized surface which had been in contact with NO at 240 Torr pressure and room temperature gave a residual weight of 72% when pumping for 5 hr at 26° and 38% after raising the temperature to 153° and pumping for 7 hr; finally 29% corresponding to 3.6 mg/g, could not be disengaged at 250°C .

These values are not considered as exactly reproducible but can be taken as a rough quantitative measure. The remaining adsorbate, especially in the case of an initially reduced surface, is assumed to be predominantly oxygen which is left behind on the surface, while NO is reduced to N_2O . The appearance of N_2O during the desorption process was shown in a separate experiment which was carried out in a small volume circulation system.

This experiment was designed to assess in what degree the irreversible chemisorption (or oxidation of the reduced surface) takes place during the chemisorption. For

this purpose, 4.74 g of reduced sample S1 were brought into contact with 352 Torr of NO at room temperature until the pressure decreased by 73%. The mass-spectrometric analysis has revealed 1.4% N₂O in the residual gas phase after 1 hr circulation and 3.1% N₂O after 10 hr circulation. Nitrogen was not found as a desorption product. From this result it is estimated that the amount of chemisorbed NO molecules which have oxidized the reduced surface sites during the chemisorption process is 1% after 1 hr and 2% after 10 hr. As the temperature increases, the degree of the irreversible chemisorption can be expected to increase. The gas adsorbed in the described experiment was desorbed at 150° and collected in a cold trap. The amount of N₂O in the desorbed gas was estimated at 16% of the total. The corresponding amount of oxygen left behind on the surface was of the order needed to oxidize the surface from Fe₃O₄ to Fe₂O₃. The sample after the experiment remained black and magnetic, while the fully oxidized sample is brown-red and nonmagnetic. This, again indicates that the oxygen is deposited only on the surface.

D. Relation Between Chemisorbed NO and Surface Iron Atoms

The establishment of this relationship is not as direct as in the case of chromia because an independent measure of the amount of transition metal ions in the surface obtained in the latter case by iodo-

metric titration cannot be readily provided. The amount of NO chemisorbed on a surface Fe atom was assessed, therefore, indirectly by 2 independent approaches.

Firstly, the amount of NO chemisorbed on 2 dilute supported samples S2 and S3 containing respectively 0.85 and 0.15 wt % Fe was measured. This was done by measuring the NO uptake at 26° for 3–4 pressure points in the 10–200 Torr range and extrapolating to the pressure corresponding to one monolayer as established for the S1 sample. In these samples every Fe atom is assumed to be exposed on the surface. As shown in Table 2, on the diluted samples the ratio of the total Fe atoms to the maximum amount of NO molecules is close to 1 Fe atom/1 NO molecule, the deviation of ~20% in dilute S3 sample is within the experimental error.

Secondly, the amount of NO molecules adsorbed per 1 iron atom in the surface can be assessed employing the previously observed 1:1 correspondence in chromia and the structural similarity between Cr₂O₃ and α-Fe₂O₃. These compounds are isomorphous and differ in their lattice parameters by only 0.5% (12). The respective maximum amounts of NO adsorbed at room temperature by pure Cr₂O₃ and Fe₂O₃ are 0.0108 and 0.0104 mmoles/m² (BET). This result confirms the same limiting capacity for NO chemisorption on iron oxide as that noted on chromia, i.e., 1 NO molecule/iron atom in the surface.

The numerical value of the NO chemi-

TABLE 2
COMPARISON OF IRON CONCENTRATION, NO ADSORPTION AND MONOLAYER COVERAGE, AND EXTRA OXYGEN INVOLVED IN OXIDATION-REDUCTION PROCESS

Catalyst designation	S1 supported	S2 supported	S3 supported	S4 unsupported
Fe wt %	8.15	0.85	0.15	Pure Fe ₂ O ₃
Total amount of Fe (mg-atom)/sample	1.148	0.1178	0.0214	10.277
Total amount of Fe (mg-atom)/g	1.46	0.152	0.0269	12.52
Fe (total) (mg-atom)	1.52	1.01	1.19	81.43
NO (max) (mmole- extra oxygen) (mg-atom NO) (max) (mmole	0.39	0.38		0.45

sorption density (6.3×10^{18} molecules/m²) is clearly within the expected range of densities of the metal ions on either Fe₂O₃ or Fe₃O₄. Thus, in α -Cr₂O₃ a chiefly exposed (0,0,1) plane has a Cr atom density of 9.8×10^{18} /m². The same Fe-atom density should also be taken for the same plane in the α -Fe₂O₃. In Fe₃O₄ we have estimated, for the 3 low index planes, the respective Fe-atom densities: (1,0,0), 8.6×10^{18} ; (1,1,0), 11.1×10^{18} ; (1,1,1), 10.7×10^{18} ; averaged value, 9.8×10^{18} . Although these densities are considerably higher than the NO chemisorption density, surfaces fully populated with one type of ions were shown by Kummer and Yao (14) to be less stable than half-populated surfaces. The NO chemisorption density falls therefore within the range bracketed by the half- and fully-populated surface ion densities, fairly close to the more probable half-populated limit.

We would like to take this opportunity to point out that in our previous publication (2) in the estimation of the chromia surface on the supported catalyst A, used also in Ref. (1), we have tacitly assumed a fully populated surface. If we assume now that the chromia surface in the sample A of Ref. (2) is populated to the same extent as the pure chromia sample, then using the limit of NO chemisorption on A of 0.55 mmole NO/g and 0.0108 mmole/m² (BET) given above, the area occupied by the chromia in the supported sample is ~ 50 m² instead of the reported 30 m². In view of the assumptions used in either of the estimations, the actual value may be somewhere within these limits.

The application of the criterion of 1 NO molecule/1 surface Fe atom to sample S1 implies that $\sim 66\%$ of the Fe atoms are exposed (Table 2) as opposed to 25% in the case of the supported chromia sample prepared in a similar manner. This means, of course, that the iron oxide is spread much more thinly. Using the limiting amount of NO chemisorption on S1 of 0.96 mmole/g and the 0.0104 mmole/m² (BET) on pure iron oxide, the surface covered in S1 by iron oxide is ~ 90 m²/g. Again, this result, predicated on the assumption that the populations on pure and supported

oxides are equal, should serve only as an approximate value.

As mentioned before, it was consistently found that the weight difference observed during oxidation-reduction was considerably higher than the amount corresponding to the bulk reduction $3\text{Fe}_2\text{O}_3 + \text{CO} = 2\text{Fe}_3\text{O}_4 + \text{CO}_2$. A comparison of the additional weight differences for the supported samples of S1 and S2, and for the unsupported sample S4 showed that the extra oxygen was present on the surface only. This conclusion follows from the data in the last line of Table 2, which were obtained gravimetrically, and is based on the fixed ratio of the extra oxygen to the amount of NO which is adsorbed at monolayer coverage. This ratio remains fairly constant, in spite of the fact that the ratio between iron in the bulk and in the surface shows considerable variations for the different samples.

For sample S1 the additional surface oxygen was also ascertained by an independent method using mass-spectrometric monitoring (2) of the gas streams in the flow oxidation of the sample by O₂-He mixtures and in the flow reduction of the sample by CO-CO₂-He mixtures (CO:CO₂ ratio of 1:3). The extra oxygen on the surfaces implies a higher oxidation state than 3 for a part of the surface Fe atoms. Higher oxidation states of iron in the bulk are known (15) but are relatively unstable. There might be a possibility that these higher oxidation states of iron are more stable on the surface as is also the case with corresponding chromium ions. We are unable to confirm this assumption at present by an independent method.

E. Comparison with the NO Chemisorption on Chromia Surfaces

Qualitatively the chemisorption of NO on the reduced and oxidized iron oxide is very much akin to that on the respective chromia surfaces, so that much of the discussion in the previous paper (1) applies here. The chemisorption on the reduced iron oxide is much stronger as manifested by the increased heat of chemisorption, larger extent of dissociative chemisorption and the

difficulty in desorption. The strong affinity of the iron atom to coordinate NO is well known (6). The fast and massive NO adsorption on the surface of iron oxide may underlie the experimental observation that the supported iron oxide catalyst exhibits the fastest rates for NO reduction by CO from among all the supported metal oxides of the first transition series (2).

As is the case for chromia, in our opinion the difference in the adsorptive behavior between the reduced and oxidized iron oxide surface is related not to the presence of a certain proportion of ferrous ions (magnetite) on the reduced surface but to the presence of the extra oxygen on the oxidized surface which exerts a strong inhibiting effect on the rate of chemisorption. Were the ferrous ions in the magnetite surface behaving differently from the ferric ions one would expect the discontinuity in the Elovich plots at around $\theta = 0.33$ instead of at 0.50 as actually noted. Further, the increase of the amount of extra oxygen on the oxidized surface obtained by cooling the sample in oxygen slows down the chemisorption of NO still more.

Thus, the capacity for NO adsorption was lowered considerably when cooling the iron oxide sample in oxygen to room temperature before evacuation and adsorption. Unsupported Fe_2O_3 adsorbed under these conditions only 30.2% of the amount of NO which was adsorbed otherwise after evacuation at 350°C. On the other hand, reduction of the oxide beyond Fe_3O_4 did not enhance its capability for NO adsorption. For example, Sample S1 which had been reduced by hydrogen at 600°C until it contained only 0.2 atoms of oxygen per atom of Fe in the bulk adsorbed only 4.9 wt % more than the limiting amount given in Fig. 1. This extra weight was most likely oxygen from NO which partly reoxidized the surface. The extra oxygen hampers the adsorption rate considerably, and at higher concentrations, it may even physically block a part of the NO adsorption sites.

The Elovich slopes of the second segment of the chemisorption plot on the reduced surface are again fairly close to the slopes of the Elovich plots on the oxidized surface.

Therefore, there is no reason to change the hypothesis advanced in Ref. (1), that the break on the reduced surface is induced by the chemisorption of NO, with the oxygen atoms pointing away from the surface, on the more energetic sites. Although rationalization for the occurrence of the break at different θ values on the supported chromia and supported iron oxide could be attempted no convincing explanation can be provided now.

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