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The Adsorption of Nitric Oxide and Carbon Monoxide on Nickel Oxide*

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Adsorption isotherms and rates for NO and CO chemisorption were measured on supported and unsupported nickel oxide samples in the 0–140°C temperature range. The isotherms are of the Freundlich type in the pressure range from 1 to 125 Torr. Monolayer coverage is attained at 110 Torr for the NO adsorption and at 530 Torr for the CO adsorption. The uptake at monolayer coverage in CO adsorption is $\sim 30\%$ smaller than the corresponding NO amount, indicating that about ⅓ of the adsorbed CO molecules are present in the bridged form. Similarly to the previously studied oxide adsorbents, there is a 1:1 correspondence between adsorbed NO molecules and Ni atoms on the surface.

The chemisorption rate of both adsorbates is described by the Elovich plots. These are more complex for CO than for NO. In the investigated temperature range, the rate of chemisorption and the heat of chemisorption are higher for NO than for CO. The rates of NO chemisorption for the transition metal oxides studied so far are in the order: iron oxide > chromium oxide > nickel oxide.

INTRODUCTION

The work presented here is an extension of the previous studies of NO chemisorption on transition metal oxides (*1*, *2*). The aim of these studies is to determine whether a correlation exists between the rates of nitric oxide chemisorption on various transition metal oxides and their catalytic activity in the reduction of nitric oxide. Another objective was to establish the limiting ratio of chemisorbed NO molecules to the available surface transition metal sites. This ratio was found to be close to unity in the case of chromium (*1*) and iron (*2*) oxides.

A further insight into the chemisorptive behavior of NO can also be gained by comparison with the chemisorption of CO on the same surfaces.

EXPERIMENTAL METHODS

A. *Adsorbents*

Two supported samples and one unsupported sample of nickel oxide were employed as the adsorbents. Both supported samples were made by impregnating Kaiser (KA-201) ⅛ in. diameter spheres with a solution of nickel nitrate, drying overnight at 120°C, and calcining at 650°C for 6 hr. One catalyst contained 6.9 wt % Ni and the other, 0.69; they were designated SN1 and SN2, respectively. Unsupported NiO (designated SN3) was prepared by decomposition of pure grade $Ni(NO_3)_2 \cdot 6H_2O$ at 500°C overnight. The studies were mainly performed on sample SN1. The chemisorption of NO on the diluted sample (SN2) and the pure NiO (SN3) served an auxiliary purpose as explained in the Discussion section. The total BET areas of SN1, SN2, SN3 were respectively 210, 180, and 3.66 m^2/g.

The oxidized state of the catalyst was

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prepared by heating to a constant weight in 10 Torr O_2 at 450°C. The reduced state was prepared by similar treatment in 10 Torr CO.

During oxidation the SN1 catalyst gained in weight 0.02 mg-atom of O/g of catalyst, meaning that less than 6% of the surface Ni atoms were present in the Ni^{3+} state. Even after heating in air at 600°C for several hours the excess oxygen content of sample SN1 was less than 0.05 mg-atom of O/g.

B. Adsorbates

Matheson research grade O_2 and CO were used without further purification. Nitric oxide was purified by the method described in Ref. (*2*) and had similar final purity.

C. Execution of Measurements

The gravimetric system built around the Cahn balance was the same as used in the previous work (*1*, *2*) with the only modification being the incorporation of a VacIon gettering pump. This pump permitted a dynamic pump-down to 5×10^{-7} Torr. The Cahn balance was also equipped with a time derivative computer for direct recording of the kinetic runs. The gravimetric apparatus was employed to measure the NO and CO chemisorption isotherms and the kinetics of CO and NO chemisorption.

The samples were initially heated in vacuum at 450°C until a constant weight was reached. Before each new oxidation or reduction treatment the sample was again held with pumping at 450°C overnight. The NO adsorption isotherms were measured on both reduced and oxidized SN1 at 26, 60, 100, and 140°C in the 2.5–110 Torr pressure range. The CO adsorption isotherms were measured similarly at 0, 26, 60, and 100°C. The CO adsorption at 140°C was too small to be measured accurately. After completion of the isothermal measurements some points were repeated to ascertain the absence of changes in the state of the adsorbing surface. The surface was considered in equilibrium with the gas phase if the weight change per hour was less than 0.2% of the amount already adsorbed. The kinetics of the NO chemisorption were studied at a pressure of 3 Torr at the same temperatures. Due to the large volume of the balance chamber (3500 cm^3) and the small amount of adsorbent (~1 g), the decrease in the adsorbate pressure was less than 10% of its initial value. Therefore, almost constant pressure and volume conditions were maintained.

D. Correction for Adsorption on Support

The amount adsorbed on a unit surface of the support, at a given temperature and pressure, was subtracted from the amount adsorbed on the supported catalyst (*1*) to obtain the value of the coverage by NO or CO of the active phase in the catalyst. The size of the correction decreased with temperature; for the SN1 catalyst, in the case of NO adsorption it was substantial at 26° (~8%), significant (3%) at 60°, and insignificant at higher temperatures. It was of course very important (~57%) in the case of the dilute SN2 catalyst at room temperature. The CO adsorption on the catalyst support was corrected for, in exactly the same manner. The correction for SN1 catalyst was ~5% at 0° and insignificant at higher temperatures.

E. Catalyst Shrinkage

From the previous experience of NO chemisorption on chromium oxide (*1*) and iron oxide (*2*), it was known that the metal oxide surface shrinks concomitantly with the alumina surface during lengthy adsorption experiments. In the case of chromium oxide and iron oxide the shrinkage was 30 and 23%, respectively. Shrinkage of active metal surface leads to the gradual decrease in total NO pickup. In the cases of iron and chromium oxides the correction for shrinkage was made by measuring the amount of oxygen that was required to oxidize the reduced surface. Since oxygen transfer in the case of nickel oxide is very small, care was taken to preshrink the SN1 surface in nitric oxide atmosphere at 450°C, before making the gravimetric measurements. The surface area of SN1 measured after this pretreatment was 210 m^2/g.

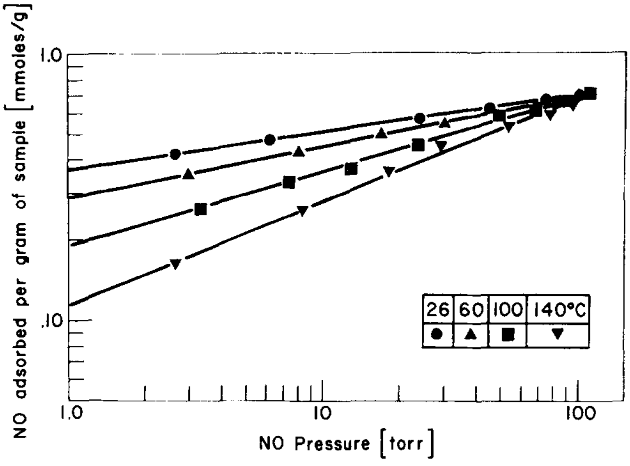

FIG. 1. Adsorption isotherms for NO on supported nickel oxide (SN1).

RESULTS AND DISCUSSION

A. Adsorption Isotherms

1. Nitric oxide adsorption isotherms. The adsorption isotherms for the SN1 catalyst are shown in Fig. 1. The plots obey the Freundlich isotherm,

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

where q is the amount adsorbed (mmoles of NO/g); p = the pressure (Torr); c and n, temperature-dependent parameters. The values of c and n are tabulated in Table 1. For supported SN1 catalyst, no difference in adsorption behavior was observed between the oxidized and the reduced samples. In this respect, supported nickel oxide differs from iron and chromium oxide for which significant differences in adsorption behavior were observed between oxidized and reduced samples. The data are treated in the same manner as previously (*1*, *2*). The amount adsorbed at monolayer coverage (q_m = 0.705 mmole/g) is given by the point of intersection of the isotherms. H_m is the heat of adsorption at $\theta = 0.37$ and is calculated directly from the exponent n of the adsorption isotherms.

TABLE 1
PARAMETERS OF FREUNDLICH ISOTHERMS FOR NO ADSORPTION ON SUPPORTED NICKEL OXIDE (SN1)

T (°K)	n	nT	$H_m = \dfrac{nRT}{(1 - rT)^a}$ (cal/g mole)	c (mmole/g)
299	6.82	2040	8980	0.361
333	5.21	1735	8751	0.285
373	3.56	1328	8234	0.189
413	2.58	1066	8571	0.115
Av H_m(cal/g mole)			8634	

[a] $r = 1.82\ 10^{-3}$ [°K]$^{-1}$. × 5

There is, however, a further refinement introduced in the present treatment of the data. The Freundlich isotherm

$$\log q = \log q_m + \frac{RT}{H_m} \log a_0 + \frac{RT}{H_m} \log p, \qquad (2)$$

as derived by the statistical approach requires constancy of H_m with changing temperatures

$$H_m = nRT = \text{constant}. \qquad (3)$$

This was the case in the NO chemisorption on the reduced chromia surface, while on the oxidized chromia surface and on iron oxide surfaces (*2*), there were deviations from this behavior. Still more marked variations of H_m with temperature are seen from the nT values in Table 1. An additional adjustable parameter r due to Halsey (*3*) can be introduced in Eq. (2), which then becomes,

$$\log q = \log q_m + \frac{RT}{H_m(1 - rT)} \log a_0 + \frac{RT}{H_m(1 - rT)} \log p, \quad (4)$$

where

$$H_m = nRT/(1 - rT) = \text{constant}. \quad (5)$$

The parameter r is so adjusted as to ensure the constancy of H_m at different temperature. The physical meaning of r is that of the coefficient which accounts for a linear variation of the adsorption entropy (or partition function) with coverage as introduced by Halsey (*3*).

In Fig. 2, the logarithmic decline of isosteric heat of chemisorption with surface coverage (θ) is shown: $H_\theta = -H_m \ln \theta$. The open circles are derived from the above relationship and the experimental value of $H_m = 8634$ cal/g mole, given in Table 1; the closed circles are derived from applying the Clausius–Clapeyron equation directly to the isotherms of Fig. 1. One has to bear in mind that, strictly speaking, the logarithmic decline of H_θ holds only in the limit of middle coverages: $0.1 < \theta < 0.8$. The fact that both the open and closed circles fall on the same curve shows the internal consistency of the data.

2. Carbon monoxide adsorption isotherms. The isotherms of CO adsorption on SN1 are shown in Fig. 3. These isotherms also follow the Freundlich type behavior. The monolayer coverage is attained at a higher pressure ~530 Torr and the amount of adsorbed CO at monolayer coverage is 0.525 mmoles/g which is lower than the monolayer coverage in NO ad-

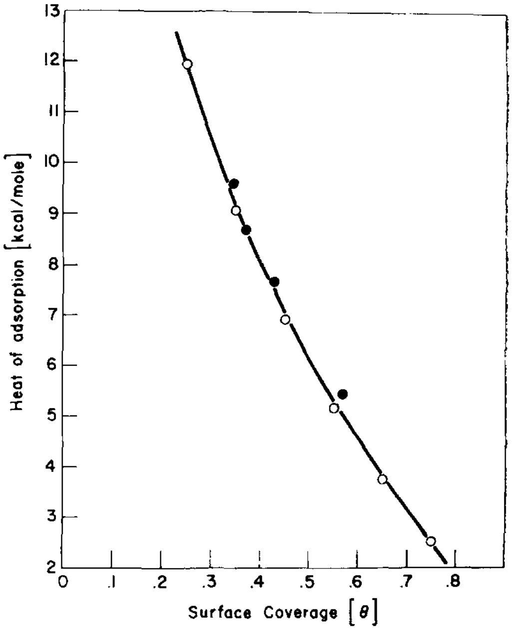

FIG. 2. Heat of adsorption vs surface coverage (θ) for NO adsorption on supported nickel oxide (SN1): (○) values calculated from: $H_\theta = -H_m \ln \theta$; (●) values calculated using Clausius-Clapeyron equation.

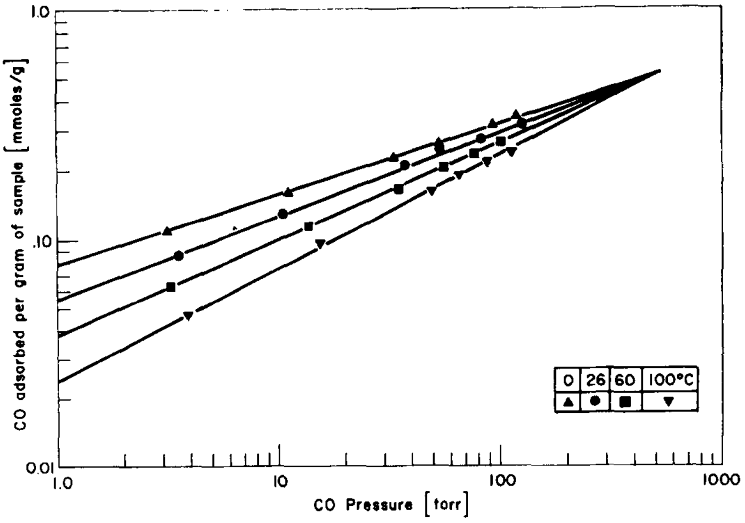

FIG. 3. Adsorption isotherms for CO on supported nickel oxide (SN1).

sorption. The parameters of the Freundlich equation for the adsorption of CO are given in Table 2. Their trends are quite similar to those measured in the NO adsorption, although the absolute values are different. Thus, again n and c decrease with temperature. The value of r which correlates the data, at a constant H_m, is 1.095×10^{-3} $[^{\circ}\mathrm{K}]^{-1}$. This value is somewhat lower than that for NO.

The change of the adsorption heat with coverage (in the range of middle coverages) conforms to the logarithmic decrease when estimated directly from the isotherms by the Clausius–Clapeyron equation, as shown in Fig. 4, where these points fall on the same curve as those derived from $H_\theta = -H_m \ln \theta$. Heat of adsorption calculated from −78 and −55°C isotherms on NiO is reported by Klier (*4*) to be 6.8 and 7.7 kcal/mole, respectively, for 5% coverage, which is in good agreement with our value ~7.6 kcal/mole for similar CO coverage.

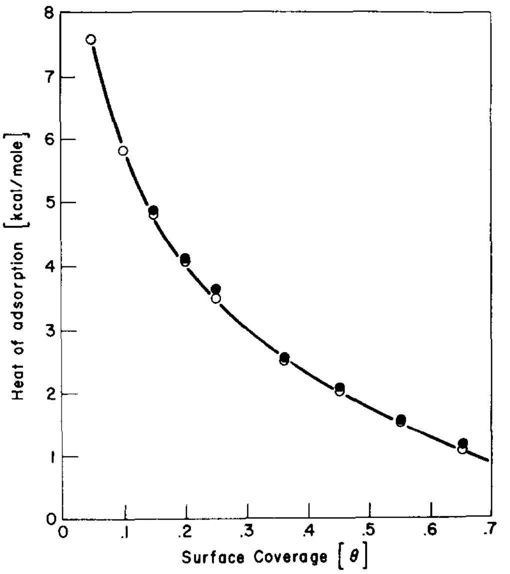

FIG. 4. Heat of adsorption vs surface coverage (θ) for CO adsorption on supported nickel oxide (SN1): (○) Values calculated from: $H_\theta = -H_m \ln \theta$; (●) values calculated using Clausius-Clapeyron equation.

B. Adsorption Rates

1. Nitric oxide. The chemisorption kinetics were followed on sample SN1. The first derivative of the weight increase was recorded automatically by the Cahn time derivative computer supplied as an accessory to the Cahn electrobalance (Ventron Corp.). The measurements were made at ~3 Torr pressure at 26, 60, 100, and 140°C.

TABLE 2

PARAMETERS OF FREUNDLICH ISOTHERMS FOR CO ADSORPTION ON SUPPORTED NICKEL-OXIDE (SN1)

T (°K)	n	nT	$H_m = \frac{nRT}{[1 - rT]^a}$ (cal/g mole)	c (mmole/g)
273	3.27	893	2521	0.078
299	2.79	834	2454	0.055
333	2.36	798	2488	0.038
373	2.02	753	2521	0.024
Av H_m (cal/g mole)			2500	

[a] $r = 1.095 \times 10^{-3}$ $[^{\circ}\mathrm{K}]^{-1}$.

As mentioned above, the large volume of the balance chamber ensured a constant pressure to within 10% during the measurement time. The results of the measurements are plotted in the coordinates of the Elovich equation in differential form

$$dq/dt = a \exp(-\alpha q), \qquad (6)$$

where q is the amount adsorbed at time t; a and α are experimental constants for a given run and depend on temperature and pressure. A sample plot at 100°C is shown in Fig. 5. On Fig. 6, the same data are replotted according to the integrated form of Elovich equation

$$q = (2.3/\alpha) \log (t + t_0) - (2.3/\alpha) \log t_0 \qquad (7)$$

where $t_0 = 1/a\alpha$ is an integration constant. Since $t_0 < t$, Eq. (7) becomes

$$q = (2.3/\alpha) \log t - (2.3/\alpha) \log t_0. \qquad (8)$$

Both plots represent two intersecting straight-line segments with the same value of q at the intersection point. The deviation of the points recorded at low times from a straight line on Fig. 6 can be corrected (*5*) by assigning a value to $t_0 = 20$ sec in the

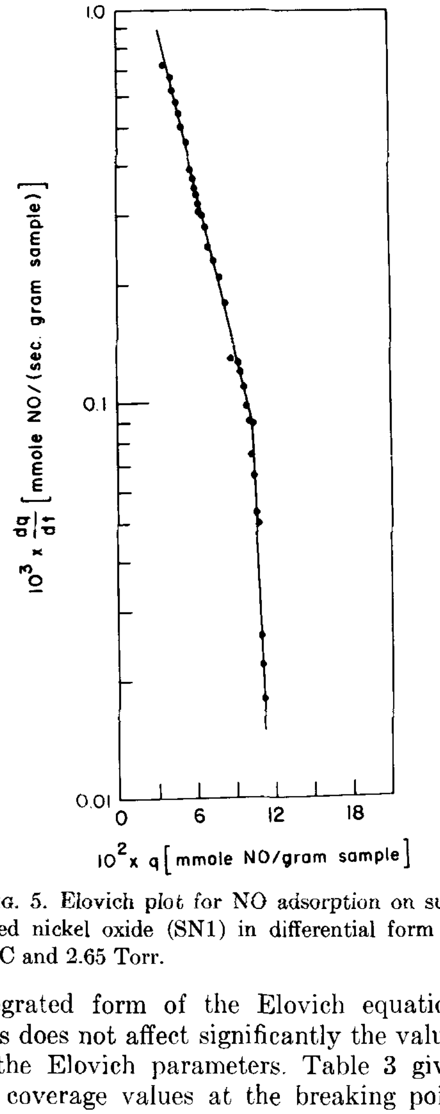

FIG. 5. Elovich plot for NO adsorption on supported nickel oxide (SN1) in differential form at 100°C and 2.65 Torr.

integrated form of the Elovich equation. This does not affect significantly the values of the Elovich parameters. Table 3 gives the coverage values at the breaking point of the Elovich plot for various temperatures in the chemisorption of NO. No significant differences were noted between the surfaces pretreated in carbon monoxide or oxygen. Henceforth, we consider both surfaces as essentially the same; and the values given in Table 3 are the averaged ones. The α parameters of both segments are also given in Table 3.

TABLE 3

COVERAGE VALUES AT THE INTERSECTION OF TWO SEGMENTS OF ELOVICH PLOTS AND α VALUES FOR THE TWO SEGMENTS OF NO CHEMISORPTION KINETICS

		[mmoles of NO/g]$^{-1}$	
T (°K)	θ	α_1	α_2
299	0.243	22	72
333	0.213	28	78
373	0.145	34	82
413	0.081	65	210

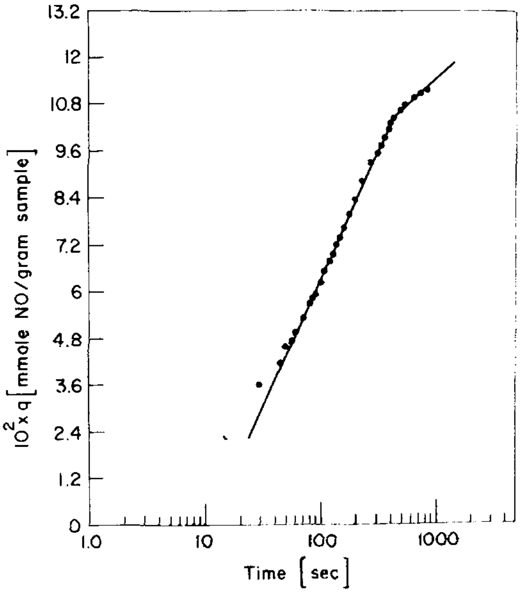

FIG. 6. Elovich plot for NO adsorption on supported nickel oxide (SN1) in integral form at 100°C and 2.65 torr.

2. Carbon monoxide. The measurements of the carbon monoxide chemisorption kinetics were made on sample SN1 in conditions similar to those for NO: at ~3 Torr pressure and at 0, 26, 60, 100, and 140°C. In Fig. 7, the results of these measurements are plotted in the coordinates of the integrated form of the Elovich equation. Here the plots are more complicated than in NO chemisorption, showing three linear segments with two breaks between them. Only one break is noted at 60°C. Table 4 summarizes the parameters of the Elovich plots of CO chemisorption. The α values for the linear segments and their ratios are listed. The ratio (α_2/α_1) remains fairly constant, ~2, with temperature change, indicating that the adsorption rate for the sites represented by the second segment is about half of the rate on the first segment sites. The (α_3/α_2) ratio, on the other hand, decreases

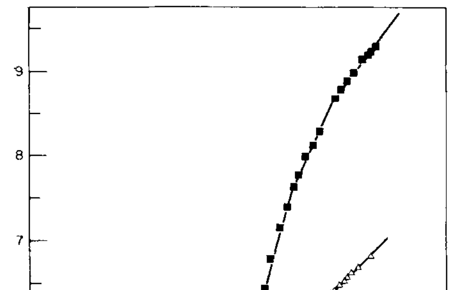

FIG. 7. Elovich plots for CO adsorption on supported nickel oxide (SN1) in integral form.

monotonically with temperature from values greater than unity to fractional values. This indicates that the rate of the chemisorption on the third segment sites overtakes the rate on the second segment sites as the temperature is increased. This implies a rather substantial activation energy for chemisorption on these sites. As shown below, the complexity of the Elovich plots for CO, compared with those for NO, can be expected because one form of adsorption of CO, the "bridged" form, does not take place in the case of NO. In general, the occurrence of multiple kinetic stages is not uncommon in chemisorption. Values of α_1/α_2 larger than and smaller than unity within the same system have been documented in Low's review article (*6*).

TABLE 4

COVERAGE VALUES AT THE FIRST BREAK OF THE ELOVICH PLOTS AND α VALUES FOR THE CO CHEMISORPTION KINETICS

		[mmoles of CO/g]$^{-1}$				
T (°K)	θ at 1st break	α_1	α_2	α_3	α_2/α_1	α_3/α_2
273	0.144	52.7	103	153	1.96	1.49
299	0.101	69.2	139	180	2.00	1.30
333	0.061	123	234	—	1.91	1.0
373	0.0356	224	494	253	2.20	0.515
413	0.0091	430	845	334	1.96	0.395

C. The Relationship Between Chemisorbed NO and CO and Surface Ni Atoms

Although, in certain cases (*7*), iodometric titration of Ni^{3+} surface atoms was employed to estimate their density, we could not use this method here as done previously for supported chromium oxides. The extent of surface oxidation–reduction was very small; and, whatever the exact valence of the exposed Ni atoms, it is very stable. Therefore, the estimate of the surface density of the Ni atoms in the SN1 sample was made, as with the supported iron oxides, by comparison with the adsorption on pure NiO (SN3) and on diluted supported catalyst SN2. On the latter sample every Ni atom is assumed to be exposed, while the average density in pure NiO can be estimated from the BET area and the known populations on the principal crystallographic planes. The limiting amount of NO adsorbed on pure NiO (SN3) is 0.0096 mmole/m^2 (BET) or 5.76×10^{18} molecules/m^2 (BET). This is within the expected range of the surface density of metal ions on the surface of NiO. The averaged value for the (1,0,0), (1,1,0), and (1,1,1) planes is 11×10^{18} Ni atoms/m^2 (*8*, *9*). If the more stable half-populated surface is assumed, the 1:1 correspondence between the chemisorbed NO molecules and the surface Ni atoms is not contradicted by experimental fact. This correspondence is further supported by the results of the diluted sample containing 0.69% Ni (SN2). Here the limiting amount adsorbed at room temperature, 0.12 mmole of NO/g, corresponds almost exactly to the total number of Ni atoms in the sample.

Table 5 compares the monolayer coverages for NO and CO on SN1 indicating clearly that the number of CO molecules accommodated by the nickel oxide surface is ~30% less than the number of NO molecules. The chemisorption of CO molecules by the occupation of 2 surface sites, the so called "bridged" form, is well documented (*10–12*). If we take the 1:1 NO:surface Ni atoms correspondence as a reference point and assume further that every "bridged" CO molecule occupies 2 surface Ni sites to the exclusion of other chemisorption bonds on the same sites, then about ⅓ of the CO molecules are in the "bridged" form occupying more than half of the Ni surface atoms. The chemisorption of NO is pictured mostly as linear, perpendicular to the surface, through the nitrogen end. The difference in the bonding behavior in the chemisorption of CO and NO is due to the antibonding electron in the latter. Thus, in nitrosyl complexes of transition metals three electrons are donated by NO to the metal atom instead of two donated by CO in the case of carbonyl complexes. The same mode of bonding is prevalent in the chemisorption of NO. A fuller account of the chemisorption bonding of NO is to be found in the review by Shelef and Kummer (*13*). The chemisorption equilibrium and chemisorption rate of both adsorbents are well described by the Freundlich and Elovich equations, respectively. In the investigated temperature range the chemisorption of CO is weaker. Thus, the heat of chemisorption at $\theta = 0.37$ on NiO is 2.5 kcal/mole for CO and 8.6 kcal/mole for NO. Monolayer coverage requires a pressure 5 times higher for CO than for NO. Further, the α parameter of the integral form of the Elovich equation, which is the inverse of its slope, is lower for NO than for CO: at 26°C, α is 22.0 and 69.2 $[\text{mmoles/g}]^{-1}$, respectively, and the difference increases with temperature, as shown in Tables 3 and 4. The relative affinity of CO and NO, with respect to the NiO surface observed here, is in full agreement with the IR study of Alexeyev and Terenin (*14*), where chemisorbed CO was displaced from NiO by gaseous NO.

TABLE 5

COMPARISON OF Ni CONCENTRATION, AMOUNT OF NO AND CO ADSORBED AT MONOLAYER COVERAGE IN SN1 SAMPLE

Ni (wt %)	6.88
Total amount of Ni (mg-atom Ni/g of catalyst)	1.17
Monolayer coverage of NO (mmole of NO/g)	0.705
" " " CO (mmole of CO/g)	0.525
Ni_{total}(mg-atom)/NO_{max}(mmole)	1.67
Ni_{total}(mg-atom)/CO_{max}(mmole)	2.22
NO(mmole) at $\theta = 1$/CO(mmole) at $\theta = 1$	1.34

D. Concluding Remarks

We refrain at the present time to make a full comparison between the chemisorption behavior of NO on the three investigated metal oxides, i.e., those of Cr (*1*), Fe (*2*), and Ni. This is because the study of the chemisorption of NO on copper oxide is in progress and the investigation on cobalt oxide is planned. Insofar, it appears that the parallelism between the chemisorption rate of NO on the three studied oxides and their relative activity in the CO–NO reaction is preserved (*15*): iron oxide > chromium oxide > nickel oxide. This is exemplified by Fig. 8, where the α parameter of the Elovich plot for the reduced form of the oxides is compared. As noted above, the lower the value of α—the higher the chemisorption rate.

Finally, it is appropriate to stress the emerging usefulness of nitric oxide as an adsorbate to be employed in the selective chemisorption for the determination of the metal surface area in a supported catalyst. Muller (*16*), in his review of the methods presently used, describes the criteria for choosing the adsorbate. The use of nitric oxide has several important advantages not offered by the presently employed adsorbates. The major advantage is that, at room temperature, NO is highly selective for transition metal atoms in the surface in a 1:1 correspondence. At this temperature, the correction for the support (Al_2O_3, SiO_2, MgO, and similar oxides) is small. There is also not much disturbing interaction, such as oxidation, with the surface. At room temperature, physical adsorption is prac-

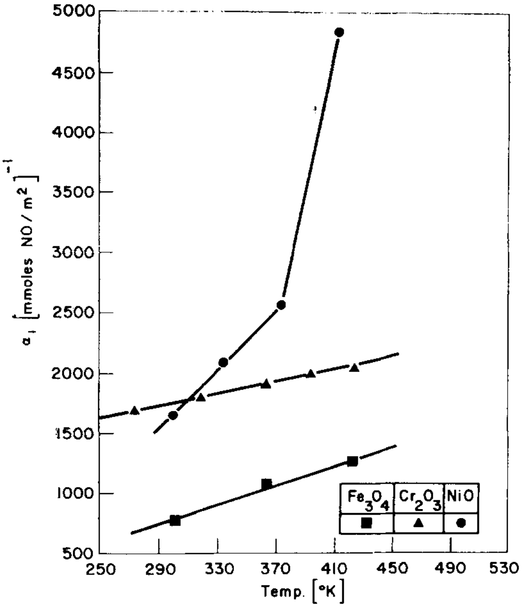

FIG. 8. Comparison of α values for the first segments of the Elovich plots for NO adsorption on reduced chromium oxide, reduced iron oxide, and nickel oxide surfaces based on unit area of active metal oxide.

tically nil and the cumbersome and inaccurate difference procedures of low temperature methods, when CO or O_2 is used are avoided. The main drawback is, of course, availability and handling facilities for NO. These are, for the most part, absent in many catalytic laboratories. The handling of nitric oxide is not more difficult, in principle, than that of carbon monoxide and in view of the demonstrated superiority for selective chemisorption the use of NO for this purpose should be seriously considered.

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