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The Adsorption of Nitric Oxide on Chromia Supported on Alumina

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Adsorptive properties of chromia supported on alumina have been studied with an electrobalance for NO as an adsorbate. Isotherms are presented in the range from −78° to 150°C for both an oxidized and a reduced surface. The isotherms are of the Freundlich type at pressures between 0.1 and 300 torr. Maximum coverage corresponds to approximately one molecule of NO per atom of chromium in the surface. The adsorption of NO can therefore be used to assess the actual chromia surface in the presence of a support material. Changes in pressure and temperature influence the coverage on an oxidized surface more strongly than on a reduced surface.

Kinetic measurements at constant temperature and pressure show a significant difference between an oxidized and a reduced chromia surface. In the first case a uniform decrease of the adsorption rate with time is observed, while in the second case a fast initial adsorption is followed by a much slower process, indicated by a sharp break in the corresponding Elovich curves. The kinetic parameters as well are influenced by temperature more strongly for the oxidized than for the reduced state.

An attempt is made to relate these chemisorption results to the catalytic behavior of supported chromia for the reduction of NO.

INTRODUCTION

Studies of the chemisorption of the "odd" molecule NO on metal and metal oxide surfaces by several different methods have been recently reported: by ESR on ZnO (*1*) and MgO (*2*); by infrared spectroscopy on transition metals (*3*), their salts or oxides (*4, 5*), and noble metals (*6*); by field emission on W (*7*); by magnetic measurements and gravimetrically on Pd (*8*), supported chromia (*9*), Al_2O_3 (*10, 11*), and SiO_2 (*12*). There exists also a body of older data obtained by volumetric and gravimetric methods (*13*). Although considerable insight has been gained into the mode of interaction of the NO molecule with the solid surface, no study directly concerned with the relation of NO chemisorption to its behavior in catalytic reactions has been reported.

In a recent study (*14*) it has been shown that chromium oxide supported on aluminum oxide is an effective catalyst for the reduction of the air pollutant NO by CO, provided that overall reducing conditions prevail. This catalytic reduction of nitric oxide is suppressed in the presence of excess oxygen. In this context it was of interest to characterize oxidized and reduced chromia surfaces and to assess differences between the two states.

Chemisorption is frequently dependent on the method of preparation or on the previous treatment of the adsorbent. Large fluctuations of the adsorbed quantities may be due to a number of undesired side effects, such as poisoning of the surface, participation of the bulk matter in some chemical reaction, or uncontrollable shrinkage of the catalyst. Chromia surfaces, in general, are found to behave well in these respects. Changes of the oxidation state of chromium can be confined to the surface, the participation of the bulk in the oxidation–

reduction process being excluded under proper experimental conditions. Surface shrinkage occurs to a certain extent, but it is possible to account for it satisfactorily. The amount of oxygen transferred during an oxidation–reduction step can be reliably measured by several methods. Results obtained using a microbalance are in good agreement with results obtained for the identical sample under somewhat different conditions, as measured by a mass spectrometer and by iodometric titration (*14*).

The adsorption measurements of NO on the chromia-alumina surfaces studied here were reproducible, and the data obtained are consistent with related results reported in the literature. It is therefore assumed that the conclusions which are drawn from these data are not limited to the particular catalyst examined here, but are meaningful for chromia surfaces in general.

EXPERIMENTAL

Adsorbents. The sample was part of the same catalyst which had been used in earlier experiments (*14*) (Sample designation A). The support consisted of 95% Al_2O_3 and 5% SiO_2 (supplied by the American Cyanamid Co.). Spectrographic analysis has shown the presence of 175 ppm Fe, 25 ppm Cu, and 2.5 ppm Mn in the support. This carrier was impregnated with a solution of chromic nitrate. The catalyst was dried and calcined for 8 hr at 600°C. The chromium content was 10%. An X-ray diffraction pattern showed the lines belonging to α-Cr_2O_3. The bare support, which was used for comparison, was subjected to the same heat treatment, after it had been washed thoroughly with distilled water. The BET area of the catalyst was measured gravimetrically by adsorption of Ar at the temperature of liquid nitrogen. The surface occupied by an Ar atom was taken as 16.9 Å^2 (*15*).

Gases. Oxygen and carbon monoxide which were used for oxidation and reduction of the chromia contained impurities amounting to less than 150 ppm (Matheson, research grade). A check by mass spectrometer showed that the gases did not pick up significant amounts of contaminants after they had been kept in the vacuum system for several weeks.

Nitric oxide containing more than 1% of impurities was further purified. The gas was first frozen at −196°C and pumped on. Less volatile components were removed by warming to Dry Ice temperature and rejecting the residue. This fractionation was repeated 5–6 times. The final product was of a blue color in the liquid state, contrary to the straw-green coloration reported by Nightingale *et al.* (*16*). The frozen solid displayed a slightly grayish tint. Mass spectrometer analysis indicated a purity of 99.8%. The major impurity was nitrogen. The mass spectrum did not show the presence of NO_2 or N_2O_3.

Apparatus. Weight changes of the adsorbent were measured by a Cahn RG electrobalance and recorded continuously. Changes of 1 μg could be observed. The microbalance was connected to a standard vacuum system which permitted dynamic pumpdown to $<5 \times 10^{-6}$ torr. A U tube containing gold bits and kept in a Dry Ice–acetone bath was used between the pump and the balance in order to eliminate mercury vapor.

A small quartz glass bucket filled with about 1 g of catalyst pellets was suspended by a quartz glass fiber from the balance arm and was counterbalanced by a similar bucket with glass beads. The sample was suspended in a quartz glass tube 60 cm long and 3.5 cm in diameter. The calculated static bouyancy was negligible because of the counterbalancing. Effects caused by convection of the gas in the sample chamber had to be considered more carefully (*17*). A series of tests, using Ar as a medium, yielded a dynamic buoyancy of less than 0.5 μg/torr for temperatures up to 150°C. A buoyancy correction was therefore not applied.

Constant temperatures at −196°, −78°, and 0°C were ensured by liquid nitrogen, Dry Ice–acetone, and water–ice baths, respectively. A stirred glycerin bath was used for higher temperatures up to 150°C. A predetermined constant temperature was maintained by an electronically controlled heater. The actual temperature of the catalyst was measured in a separate test. For this purpose the tip of a thermocouple was placed at the location of the sample. The temperature of the sample was found to deviate by less than 1°C from the temperature of the bath.

Conditioning of surface. The sample reached a constant weight after 2 weeks at 450°C in a vacuum, losing about 5% of its weight during this period. For the reduction, the sample was heated to 450° while pumping, exposed to CO for 1 hr (5 torr in a volume of 3.5 liters) and then evacuated for 30 min. Finally the sample was kept under 5 torr of CO for 14 hr. No further reduction was noted upon prolonging or repeating this process. The sample chamber was evacuated and cooled to the desired temperature and the measurements commenced after the balance had indicated a change of less than 0.03 mg/hr. For the oxidation at the same temperature a similar procedure was followed using 5 torr of oxygen.

Sintering. Over the long duration of the measurements a substantial shrinkage of the chromia surface (up to 30%) was noted, as indicated by the decrease in the amount of oxygen which was transferred during an oxidation–reduction step. A determination of the total chromia–alumina surface by the BET method, after completion of the adsorption measurements, showed that the alumina surface had shrunk concomitantly with the chromia surface. This observation was surprising since the sample temperature was never raised above 500°C and remained at all times well below the temperature of the original calcination. A decrease of the chromia surface by 14% was found during previous NO reduction experiments, but no contraction of the alumina surface was detected (*14*). Possibly the presence of a high NO concentration aided and intensified the sintering process. A similar influence was observed during the NO adsorption on nickel and iron films for which surface shrinkage was noticeable even at —78°C (*18*).

Execution of measurements. Adsorption isotherms were measured in a random fashion, in order to minimize the possibility of systematic errors introduced by aging of the catalyst. Measurements on reduced and oxidized surfaces were alternated for this purpose, and a systematic change of temperature in the succession of the isotherms was avoided. In addition some points of each isotherm were repeated at different times.

The amount of oxygen which was needed for the oxidation of a reduced surface under the conditions described above, was taken as a direct measure for the actual chromia surface and a correction was applied correspondingly to allow for the shrinkage. Without this correction a noticeable discrepancy of some of the adsorption results which were obtained under seemingly identical conditions would have resulted.

The adsorption process continued at a very low rate for a long time, and the establishment of adsorption equilibrium was difficult. Solbakken and Reyerson (*10*) observed similar behavior for NO adsorption on an alumina gel. They found significant adsorption even after 100 days. A comparative test proved that slow adsorption occurs on the surface of the bare alumina support in the same fashion as it does on the chromia-alumina surface. This fact was especially evident at low temperatures and high pressures. It was therefore assumed that the adsorption which was observed after 24 hr occurred on the alumina rather than on the chromia surface. Adsorption measurements were usually continued for 6 to 24 hr, until the amount adsorbed per hour was less than 0.2% of the quantity already adsorbed. The amount of nitric oxide which was adsorbed on alumina, determined from the NO adsorption of the bare support under equal conditions, was subtracted from the adsorbed portion. The correction was substantial for the isotherms at —78° and at 0°C for NO pressures above 1 torr. It was still noticeable at 90°C, but not at 150°C.

Rates of adsorption were measured at −78°, 0°, 45°, 90°, 120°, and 150°C on oxidized and reduced surfaces. The usual pressure of NO was 3 torr. The pressure decreased by less than 10% during the

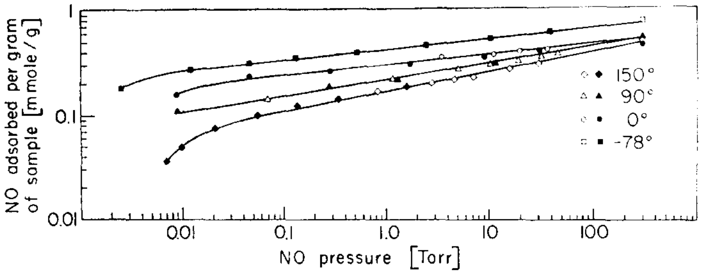

FIG. 1. Adsorption isotherms for NO on supported chromia in the reduced state.

measurements. The increase of the sample weight was continuously registered by a recorder. The rate was given by the slope of the recorder trace. The kinetics of the adsorption was followed until about 60–70% of the total amount, as given by the static isotherms, was adsorbed. The run in each case lasted usually for about 3 hr. Measurements were repeated at least twice under the same conditions.

EXPERIMENTAL RESULTS

The initial total surface of the chromia-alumina sample, determined gravimetrically from the adsorption of argon at −196°C, was 194 m^2/g. The unit of adsorption which is used here is "millimoles of NO per gram of catalyst in its initial state" (mmoles/g). Adjustment for surface shrinkage is always taken into account. The notation "per gram" is therefore equivalent to "per 194 m^2."

The amount of oxygen required to oxidize a sample which had been reduced under the stated conditions (at 450°C) was 0.62 mg atom oxygen/g catalyst. It has been shown previously for the same sample that this oxidation corresponds to an average oxidation state of 5.5+ for the surface chromium [Fig. 8 in ref. (*14*)]. Assuming that the surface chromium in the reduced state is present in the 3+ state it follows, as the oxygen atom carries 2 charges, that the chromium concentration in the surface is $0.62 \times 2/(5.5 - 3) = 0.5$ mg atom Cr/g. It is worth noting that Weller and Voltz (*19*) have reported previously that chromium is not reduced to the Cr^{2+} state in a static apparatus, presumably because of residual amounts of oxygen in the system.

Isotherms

The adsorption of NO on reduced and oxidized surfaces is shown in Figs. 1 and 2 for four different temperatures. Open and filled symbols on the isotherms indicate separate runs between which the surface has been subjected to at least one oxidation–reduction cycle. The two kinds of symbols illustrate the reproducibility of the measurements. The dashed lines in Fig. 2 represent data which have not been corrected for NO adsorption on the alumina support, showing that this correction is important. The same correction was applied

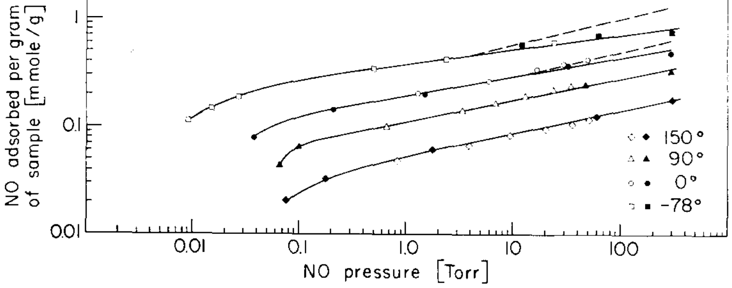

FIG. 2. Adsorption isotherms for NO on supported chromia in the oxidized state.

to the data in Fig. 1 but the dashed lines are omitted for the sake of clarity.

The experimental results are best described by Freundlich isotherms, which correlate, at a given temperature, the adsorbed quantity q of NO and the pressure p

$$q = cp^{1/n} \tag{1}$$

where c and n depend on the temperature only. This isotherm is amply described in the standard literature, see e.g., Hayward and Trapnell (*20*). The basic test for the Freundlich isotherm is to determine whether, for logarithmic coordinates, q changes linearly with p. Figures 1 and 2 show that this relationship is true for at least a pressure range from 0.1 to 300 torr NO. The deviation of the isotherms from straight lines for pressures below 0.1 torr (coverages below 0.2) is expected. Thermodynamic considerations show that n depends on the interaction between adsorbed molecules. If this interaction is negligible, e.g., on sparsely covered surfaces, an adsorptive behavior according to Henry's law [Eq. (1) for $n = 1$] should be observed. The isotherms in Figs. 1 and 2 are consistent with this consideration, that is with a slope $1/n = 1$ in a log q versus log p diagram.

Adsorption data which can be described by Freundlich isotherms yield coefficients $n(T)$ and $c(T)$ which usually decrease as the temperature increases. As a rule, n is greater than 1, provided that the mutual interaction of the adsorbate molecules results in a repulsive force (*20*). These intrinsic features of the Freundlich isotherms are confirmed for the NO adsorption on reduced and oxidized chromia surfaces, as shown in Table 1.

TABLE 1

Coefficients of Freundlich Isotherms

T (°K)	n	nT	c (mmole/g)	log c
		Reduced Surface		
195°	10.86	2118	0.420	−0.377
273°	10.31	2814	0.299	−0.524
363°	7.07	2565	0.232	−0.634
423°	5.57	2356	0.167	−0.777
		Oxidized Surface		
195°	7.19	1402	0.362	−0.441
273°	6.12	1671	0.189	−0.724
363°	4.96	1801	0.108	−0.967
423°	4.74	2003	0.0525	−1.280

A more demanding test of the Freundlich isotherm requires that the family of isotherms, with temperature as a parameter, intersect in a common point at monolayer coverage. This is the consequence of the statistical derivation of the isotherm whose final form (*20*) is*

$$\log q = \log q_m + (RT/H_m) \log a_0 + (RT/H_m) \log p \tag{2}$$

Monolayer coverage q_m at any temperature T is reached at $p = 1/a_0$; R is the gas constant, and H_m a temperature-independent constant.

A comparison of the logarithmic form of Eq. (1) with Eq. (2) leads to the simple relations

$$nT = \frac{H_m}{R} = \text{const.} \tag{3}$$

and

$$\log c = \log q_m + \frac{RT}{H_m} \log a_0 \tag{4}$$

which are used subsequently to compare the experimental results with the theory.

Figure 1 shows clearly that with the exception of the isotherm at −78°C the plots for the reduced surface tend to a common point. Table 1 shows that the product nT can be considered as constant, if an experimental uncertainty of 10% for determining n is accepted, exempting the isotherm at −78°C. Equation (4) holds if an experimental error of 3% is assumed for log c. On the other hand the isotherms on the oxidized surface are nearly parallel and the experimental data show considerable disagreement with Eqs. (3) and (4).

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* A remark to avoid confusion in the notation is in order. We use throughout q as the amount adsorbed in mmoles/g, while Hayward and Trapnell use q in the Elovich equation in a similar sense, but in the treatment of isotherms to denote heats. The values q and q_m in their notation for the Freundlich isotherm have been replaced here by H and H_m, respectively.

We deduce from this behavior that the adsorption of NO on the reduced chromia surface in the 0–150°C range follows the Freundlich isotherm. With regard to the oxidized surface, the isothermal behavior is well described by Eq. (1) but no conformity with the assumptions underlying the derivation of the isotherm is found. It is worthwhile to note in passing that the data for the whole range of pressures do not produce linear plots in q–log p coordinates.

From the point of intersection in Fig. 1, the monolayer coverage on the reduced surface is taken to be 0.55 mmoles/g. This corresponds to 1.1 NO molecules per chromium atom in the surface, taking 0.5 mg atom Cr in the surface per gram of sample (*14*).

There is no straightforward estimate for the oxidized surface as the coverage is strongly dependent on temperature. An attempt to estimate the monolayer coverage using Eq. (4), i.e., by plotting the values of log c from Table 1 versus T and extrapolating to $T = 0$, yields the improbable value of 1.95 mmoles NO/g, i.e., about 4 NO molecules per chromium atom in the surface.

The adsorbed NO could be disengaged from the oxidized surface without decomposition by pumping while raising the temperature to 200°C. This was judged by the return of the sample weight to its original value. The upper limit of the weight retained during pumping at 250°C on the reduced surface was 5% of the total amount adsorbed. This variation was conceivably oxygen used up for oxidation of the reduced surface during heating. Since oxygen constitutes only about one-half of the mass of NO, the assessment of desorbable NO on the reduced surface yields more than 90%. Although no desorption isotherms were measured, trial runs indicated strong hysteresis, in particular on the reduced surface. For example, starting at −78°C with a coverage corresponding to a monolayer, the NO coverage was decreased to 80% after pumping for 7 hr. After the sample had been warmed up to 0°C, it took 16 hr to reach 60% coverage. Continued evacuation for 2 hr at 175°C removed the adsorbate down to 28%. At approximately 250°C the balance indicated that less than 5% of the adsorbed mass remained on the surface.

Kinetic Measurements

The adsorption rates on both surfaces are well described by the widely employed Elovich equation. Because the Elovich equation fails at high coverages, rate measurements were terminated when about 2/3 of the available sites were covered.

The differential form of the Elovich equation

$$dq/dt = a \exp(-\alpha q) \tag{5}$$

describes the rate of adsorption as a function of the amount q which is adsorbed at time t; a and α are coefficients which are dependent on temperature and pressure. The integrated form is

$$q = (2.3/\alpha) \log (t + t_0) - (2.3/\alpha) \log t_0 \tag{6}$$

where $t_0 = 1/a\alpha$ is an integration constant. There is a controversy (*21*) about whether the differential or integral form should be employed in the evaluation of the experimental data. The data here were therefore treated both ways. In all cases t_0 was determined to be much smaller than the time needed for the weighing system to come to rest after the jolt caused by the admission of the gas, which was about 15 sec. Hence the time of the first reliable measurement is much larger than t_0 and (6) is simplified to

$$q = (2.3/\alpha) \log t - (2.3/\alpha) \log t_0 \tag{6a}$$

Typical Elovich plots according to Eqs. (6a) and (5) are given both for the oxidized and reduced surface in Figs. 3 and 4, respectively. Comparison of the figures shows the essential equivalence of both methods of plotting. The respective slopes $1/\alpha$ and α are in good mutual agreement, those obtained from the differential equation giving a somewhat larger scatter.

The most important features of Figs. 3 and 4 are a much faster rate of chemisorption on the reduced surface and a sharp

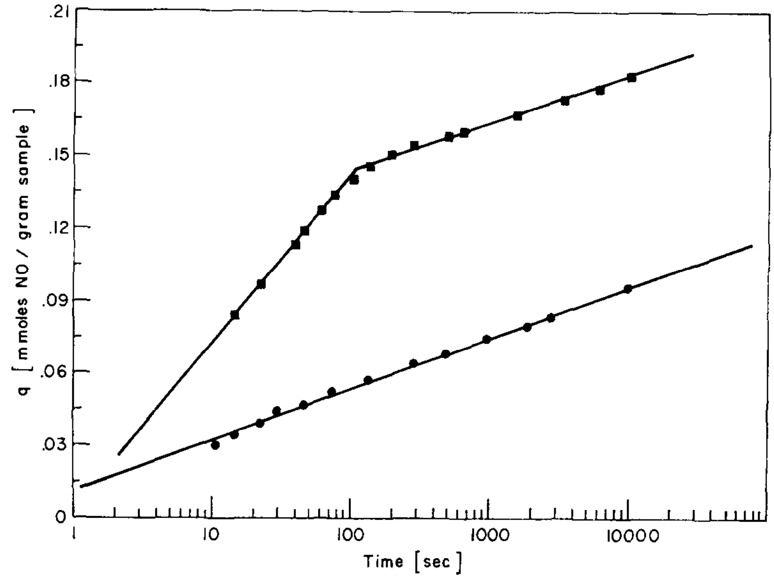

FIG. 3. Elovich plots for NO adsorption at 45°C and 2.8 torr for supported chromia in the oxidized (●) and reduced (■) state.

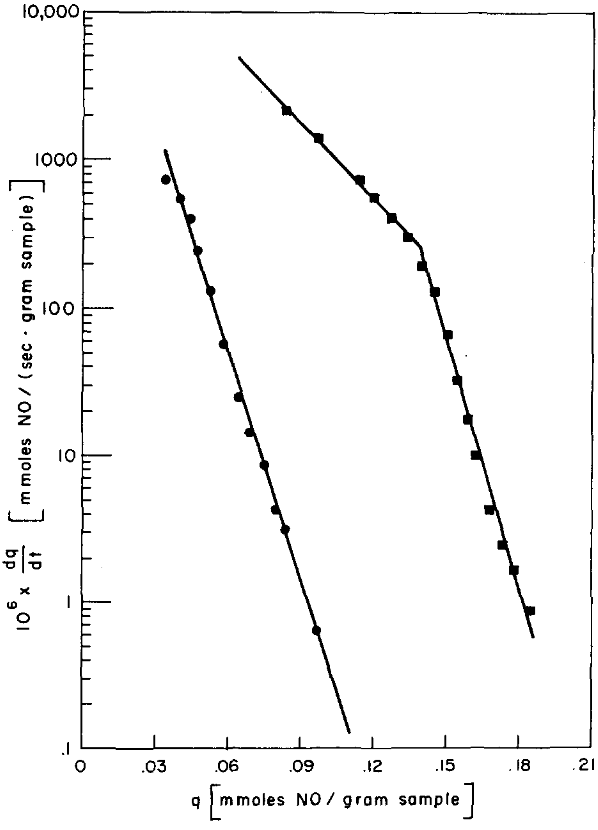

FIG. 4. Data from Fig. 3 plotted for log (dq/dt) versus q.

TABLE 2
INTERSECTION OF LINE SEGMENTS IN ELOVICH PLOTS FOR REDUCED SURFACE

T (°C)	Time (sec)	Coverage (mmoles NO/g)
0°	150	0.149
45°	130	0.140
90°	125	0.132
120°	160	0.138
150°	190	0.132

break in the Elovich plots for the same surface. Breaks in the Elovich plots were noted on the reduced surface at all temperatures in the range from −78° to 150°C. The coordinates of the intersection of the two straight-line segments are given in Table 2.

On the other hand the Elovich plots of the adsorption rate on the oxidized surface were smooth in all cases with the exception of the plot at −78°C, as shown in Fig. 5. The behavior at −78°C was different from that in the temperature range from 0° to 150°C, most probably due to copious physical adsorption as observed by Solbakken (*11, 12*) and also here (see Fig. 2). For this reason the kinetic evaluation omits the data obtained at −78°C.

The change of the coefficient α with temperature can give some information on the temperature dependence of the chemisorption process. Figure 6 shows that α increases rather steeply with temperature above 300°K, while the coefficient α_1 and α_2 of both linear segments, relating to the reduced surface and shown in Fig. 7, increase only slightly. From Eq. (5) it is evident that the increase of α at a given coverage results in a decrease of the adsorption rate. Hence, it may be deduced that the temperature coefficient of the adsorption is negative for both surfaces, more so for the oxidized surface. It is possible to express this coefficient numerically using an Arrhenius plot of log α against $1/T$ as done by Shereshefsky and Russel (*22*). The values of the temperature coefficients derived thereby are −1.4 kcal/mole for the oxidized surface and −0.3 kcal/mole for either linear segment of the Elovich plot pertaining to the reduced surface. Table 3 shows the actual measured rates at a constant coverage of 0.055 mmoles NO/g, which corresponds to a coverage $\theta = 0.1$, on the reduced surface. It emphasizes the considerable difference between the chemisorption rates on oxidized and reduced

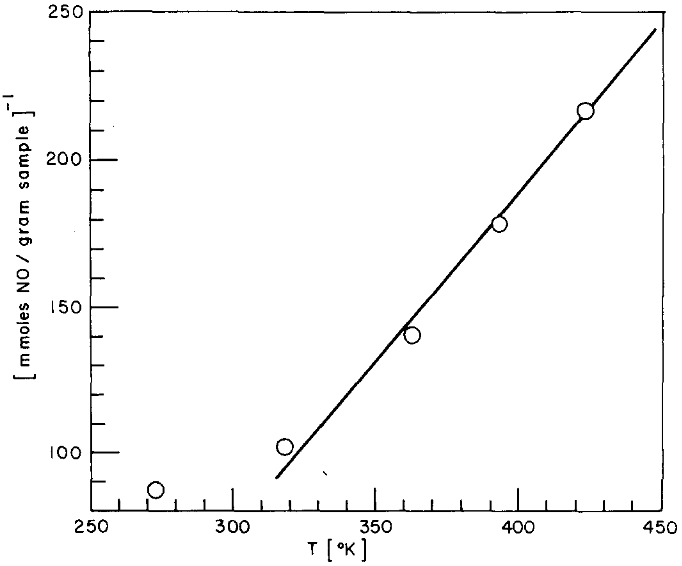

FIG. 5. Elovich plots for NO adsorption at −78°C and 2.8 torr for supported chromia in the oxidized (●) and reduced (■) state.

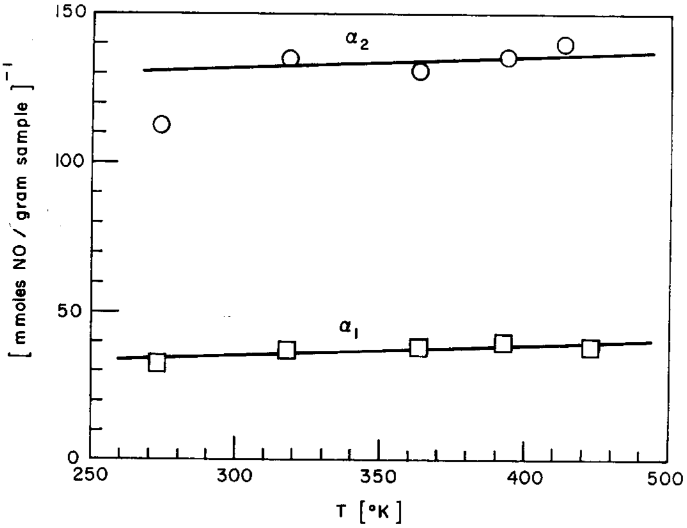

FIG. 6. Temperature dependence of α from Elovich plots of oxidized chromia surfaces (2.8 torr NO).

surfaces in this range of coverages, and also that the difference increases with temperature. The rates depend on the exponential factor α as well as on the pre-exponential factor a, which can be considered as the rate of adsorption on the bare surface. It is determined by the ordinate intercept of the Elovich plot. The initial rate for the reduced surface assessed in this manner exhibited a slightly positive temperature coefficient. Such an extrapolation was unwarranted on the oxidized surface due to the very steep slope.

DISCUSSION

The density of chromium atoms on the predominantly exposed crystal face of α-Cr_2O_3, that is assumed to be the 0001 plane, was estimated by McIver and Tobin (*23*) as 9.8×10^{18} atoms/m^2. The adsorption of one molecule of NO per surface chromium atom (within 10% accuracy) on the reduced surface is consistent with the geometrical picture that the NO molecule is not adsorbed in the "lying down mode." The maximum amount of NO which can be

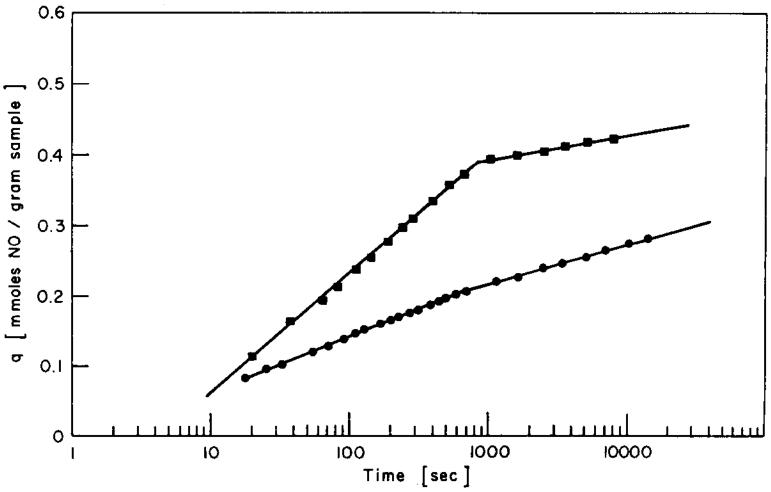

FIG. 7. Temperature dependence of α_1 (first line segment) and α_2 (second line segment) from Elovich plots of reduced chromia surface.

TABLE 3

Comparison of Specific Rates of Adsorption at Constant Coverage Corresponding to 0.055 mmoles NO/g (pressure ~3 torr)

T (°C)	Rate of adsorption × 10^5 (mmoles NO/sec × g)	
	Oxidized surface	Reduced surface
0°	1550	5700
45°	92	6600
90°	87	2950
120°	26	2600
150°	13	8900[a]

[a] Obtained by extrapolation beyond the range of experimental data.

arranged in this mode has been estimated by Yates and Madey (*7*) to be about 8×10^{18} molecules/m^2 only. These authors have also concluded that NO chemisorbs on tungsten in a "standing up mode." There exists also other evidence that NO is adsorbed mainly with the molecular axis perpendicular to the surface and through the nitrogen end (*3, 4*).

We deduce from the experimental results that the adsorption on oxidized and reduced chromia surfaces may be regarded as chemisorption. Thus the process is slow, specific with respect to the chromium atoms in the surface, and occurs at temperatures far removed from the critical temperature of NO (−96°C). The isosteric heats of adsorption obtained by application of the Clausius-Clapeyron equation are reliable only at high coverages where the requirement of reversibility is satisfied. The heat of adsorption derived in this manner from the isotherms below 100°C at a coverage of 0.3 − 0.4 gives 5.5 kcal/mole for both surfaces. This is not greatly different from the values for physical adsorption on a number of surfaces (*8, 12, 24*) which fall in the range from 3.7 to 4.0 kcal/mole. Indeed, in the region of high coverages the heat of chemisorption may be expected to be low, because the Freundlich isotherm, to which the adsorption data conform, requires a sharp, logarithmic drop in the heat of chemisorption (*20*) according to

$$H_\theta = -H_m \ln \theta \qquad (7)$$

where H_θ is the heat of chemisorption at coverage θ, and H_m is the constant earlier employed in Eq. (2). The numerical value of H_m equals that of H_θ when $\ln \theta = -1$ or when $\theta = 0.37$. The average value of $H_m = nRT$, obtained in the range from 0° to 150°C for the reduced surface from the data in Table 1, is 5.1 kcal/mole, in good agreement with that directly derived by the Clausius-Clapeyron equation in the same range of coverages. Using relation (7) for extrapolation to lower coverages one obtains $H_\theta = 11.7$ kcal/mole at $\theta = 0.1$ for the reduced surface, which is close to that measured at a similar coverage on a palladium surface (*8*). Clearly, no extrapolation to very low coverages is permissible, as in this case $H_\theta \rightarrow \infty$. The observed increase of H_m with T on the oxidized surface is possibly associated with the change of the "monolayer coverage" with T. At higher temperatures the low-energy sites do not chemisorb NO at any pressure and the "monolayer coverage" decreases with T. As the temperature is increased, a given fraction of adsorbed NO is shifted to adsorption sites which represent on the average an increased heat of adsorption, thus increasing H_m.

The negative temperature coefficient of the chemisorption rates is a frequently observed phenomenon which is due to the complexity of the changes taking place on the surface during chemisorption. Usually no mechanistic significance can be attached to this observation (*25*). Nevertheless, it must be mentioned in this context that the negative temperature coefficient in the case of NO chemisorption seems to be the rule rather than the exception (*8, 11*). An explanation which has been advanced in this matter for the adsorption of NO on alumina gel (*11*) and on Pd (*8*) is based on two consecutive adsorption steps. However, such a scheme is not unique, as a surface diffusion-controlled adsorption can also result in a decrease of the adsorption rates with increasing temperature (*26*). Such a mechanism involves a fast adsorption on a small number of preferred sites. The majority of adsorption sites can be filled more easily via surface diffusion than by collisions with NO molecules from the gas phase. The diffusion flux which determines the NO uptake depends on two factors: the concentration of NO molecules on the preferred sites and the specific diffusion rates across the surface. Each term contains an energy exponent. The concentration term decreases with temperature according to the heat of the first adsorption step, while the second factor increases correspondingly, according to the activation energy of the diffusion process. Consequently, the adsorption rates decrease as the temperature increases as long as the heat of adsorption for the preferred sites is larger than the activation energy of diffusion. The practical significance of the negative temperature coefficient is its relevance to the catalytic process.

The adsorption of NO on chromia is slow, in spite of the fact that there is no experimental evidence for a substantial energy of activation. One is therefore led to the conclusion that the adsorption is associated with a very small pre-exponential factor. Solbakken and Reyerson came to the same conclusion when investigating the adsorption of NO on alumina gel (*11*); they calculated an extremely small transmission coefficient for this case.

The breaks which have been observed in the Elovich plots are sharp and occur at all temperatures in the narrow range of 0.13–0.15 mmoles NO/g which corresponds to 0.24–0.27 of the monolayer coverage. The slope of the second linear segment of the Elovich plots for the reduced surface is roughly the same as that for the oxidized surface. The break can be interpreted as evidence for two distinct populations of sites. Both populations may be present on the outgassed surface or the second, less energetic population may be induced by adsorption on the most energetic sites. The adsorption data alone do not provide a choice between these possibilities. A speculative argument can be made in favor of an induction of the second, less energetic population during the adsorption process. The oxidation–reduction results show that every atom in the surface undergoes an oxidation state change. Thus, the environment of every surface atom should be affected by the reduction and one would not expect *a priori* that the number of the reduced sites is restricted to about ¼ of the surface. The similarity of the Elovich slopes of the second segment on the reduced surface to that on the oxidized surface, on the other hand, suggests that the corresponding energy barriers for the adsorption are not too different. One can visualize a situation whereby a reduced surface, covered to about ¼ θ with NO molecules, which are adsorbed through the nitrogen end, behaves with respect to chemisorption similar to an oxidized surface. The existence of two distinct populations of chemisorption sites on the reduced surface does not disturb the course of the Freundlich isotherm. This can be understood since the variation of the heat of chemisorption with coverage takes place in a very narrow range after ¼ of the available sites have been covered. Indeed, the isosteric heats evaluated in this range are the same for both surfaces, as mentioned above.

The chemisorption rate is relevant to the catalytic process only insofar as it may determine the overall rate of the latter. To answer this question, the formal kinetics of the overall process must be known, which is not the case at present. Were the chemisorption kinetics rate-determining, then, judging from the data of Table 3, one would expect the reduced surface to be a far superior catalyst than the oxidized surface. This is indeed the observed behavior (*14*). It is also clear that the chemisorption rate gap between the different surfaces will increase as the temperature is increased to that employed in the catalytic work (200–300°C).

A comparison was made between the chemisorption rates on the reduced surface, tabulated in Table 3, and the rates of the catalytic reaction between CO and NO under overall reducing conditions, using previously measured data on the identical catalyst (*14*). Both rates turn out to be of similar order of magnitude in the temperature range from 100–150°C, where a direct comparison can be made at pressures of a few torr of NO. The result shows that the chemisorption of NO can not be ruled out as the rate-limiting step. More definite conclusions are unwarranted in view of the fact that the state of the surface in the chemisorption studies involving NO only may not be the same as in the catalytic reaction where other gaseous species also interact with the surface.

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