Pulse Studies of the Adsorption of Nitric Oxide on Iron Oxide Surfaces

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Moment analysis of the effluent peaks from input pulses to a packed column was used to study the activated adsorption of NO on Fe_2O_3 (14.2% Fe_2O_3 on Al_2O_3) at 370–410°C. The adsorption equilibrium constant at 400°C was 3.2 cm^3/g and the heat of adsorption in the temperature range 370–410°C was 12 kcal/mol. The adsorption equilibrium constant of NO decreased with time during flow of helium through the bed of particles. By auxiliary experiments with N_2O pulses it was confirmed that this decrease was due to desorption of atomically adsorbed oxygen. The combination of NO and N_2O pulse data provided evidence that NO was adsorbed on sites involving the adsorbed oxygen. Kinetic analysis of the data for the decrease in NO adsorption with time of helium flow suggested that the desorption of atomic oxygen was a second-order process with an activation energy of about 47 kcal/mol.

NOTATION

$C(z, t)$ Concentration of tracer component as a function of bed length and time, mole/cubic centimeter

E_d Activation energy for desorption of atomic oxygen from surface of Fe_2O_3 particles, kilocalories/mole

ΔH Enthalpy change of adsorption, kilocalories/mole

K_A Adsorption equilibrium constant for NO on Fe_2O_3, cubic centimeters/gram

t Time, seconds, t_0 = pulse injection time; t_d = residence time in the dead volumes between pulse injection and bed entrance and between bed outlet and detector

v Interstitial velocity of the gas in the interparticle void space of the bed (given by the flow rate divided by the cross-sectional area of the column and by the void fraction, α, centimeters/second

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z Length of packed bed measured from inlet, centimeters

α Interparticle void fraction in the bed

β Intraparticle void fraction of the adsorbent particles (Fe_2O_3/Al_2O_3)

δ_0 Defined by Eq. (2)

θ Fraction of particle surface covered by oxygen atoms

ρ_p Apparent particle density, grams/cubic centimeter

ρ_t True density of solid, grams/cubic centimeter

μ_1 First absolute moment, seconds

INTRODUCTION

The importance of removing nitrogen oxides from combustion gases has stimulated interest in the adsorption of NO on porous solids such as transition metal oxides. Studies of NO adsorption on partially reduced oxides have been carried out by means of several techniques, ESR, IR and direct volumetric or gravimetric mea-

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surement (1–4), but little information is available for fully oxidized adsorbents, particularly for activated adsorption at high temperatures. Since exhaust gases normally contain some oxygen, adsorption studies on oxidized materials is important. The results reported here are for adsorption on iron oxide (Fe_2O_3) as a function of extent of oxidation, that is, the amount of chemisorbed oxygen on the surface of the absorbent.

Anderson (5) and Markvart (6) observed a large increase in catalytic activity for the reaction between NO and NH_3 when oxygen was introduced. This has been confirmed by current research of Professor Echigoya and his colleagues at Tokyo Institute of Technology by studies of the same reaction on Cr_2O_3/Al_2O_3 with oxygen pretreatment. These findings suggest that NO is adsorbed on surface oxygen, forming an NO_2-like complex, i.e.,

$$NO(g) + O \cdot X \rightleftarrows NO_2 \cdot X$$
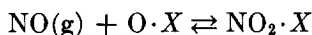
The data that follow confirm that NO is adsorbed on surface oxygen and provide information on the kinetics of desorption of the surface oxygen.

Traditional methods for adsorption studies, which often involve relatively large exposure times, involve difficulties due to reaction to NO_2 and its desorption into the gas phase and to changes in surface conditions due to recombination and desorption of some of the surface oxygen atoms. Recently developed chromatographic, or pulse, techniques for measuring adsorption parameters, such as the equilibrium constant, avoid these problems since the retention time of NO pulses is very short, the order of 10 sec. In addition, by injecting single pulses of NO into a packed bed of catalyst particles at different times, it is possible to study the kinetics of desorption of the surface oxygen. This is possible because oxygen is desorbed during the flow of helium between NO pulses. We have used the chromatographic technique to evaluate adsorption equilibrium constants for NO on Fe_2O_3/Al_2O_3 over the temperature range 370–410°C. The procedure was to analyze the first moment of the response peak from a bed of catalyst particles when a pulse of 0.6% NO in helium is injected into the feed stream.

MOMENT METHOD OF ANALYSIS

When a pulse of adsorbable gas is introduced into an inert carrier gas at the entrance to a bed of adsorbent particles, the adsorption equilibrium constant can, under certain restrictions, be related to the first absolute moment of the response peak at the exit of the bed. The derivation of the theory is given in detail elsewhere (7,8). The most important restrictions are that the bed be isothermal, the pressure drop be small compared to the total pressure, radial variations in velocity in the bed be negligible, the adsorption be reversible and rapid, and all mass transfer processes be linear. The last requirement means that the rate of adsorption is first order or that the adsorption isotherm is linear. For the rapid, reversible restriction to be met, all the tracer material in the input pulse should appear in the response pulse, that is, the zeroth moment should be unity.

With these restrictions it has been shown (8) that the observed first absolute moment is given by

$$\mu_1 = (z/v)(1 + \delta_0) + (t_0/2) + t_d \quad (1)$$

and

$$\delta_0 = \left(\frac{1 - \alpha}{\alpha}\right)\beta\left[1 + \frac{\rho_p}{\beta} K_A,\right] \quad (2)$$

where z, v and t_0 are the length of the packed bed, interstitial gas velocity, and the injection time of the pulse, respectively, and K_A is the adsorption equilibrium constant. For an inert (nonadsorbable) tracer

such as nitrogen, $K_A = 0$ and Eqs. (1) and (2) reduce to the form

$$(\mu_1)_{N_2} = \frac{z}{v}\left(1 + \frac{1-\alpha}{\alpha}\beta\right) + \frac{t_0}{2} + t_d. \quad (3)$$

If Eqs. (1) and (2) are combined, and applied to adsorbable NO, the difference between the moments of NO and N_2 does not involve the residence time, t_d, in the dead volumes and is given by

$$\Delta\mu_1 = (\mu_1)_{NO} - (\mu_1)_{N_2}$$
$$= \frac{1-\alpha}{\alpha}(\rho_p K_A)\frac{z}{v}. \quad (4)$$

This result shows that at a fixed temperature the difference in first moments is directly proportional to z/v. Hence, a plot of first moments measured for different gas velocities should be a straight line, if the coordinates are $\Delta\mu_1$ and z/v. The slope of the line determines the adsorption equilibrium constant.

The first absolute moment can be calculated for both NO and for N_2 from the measured response peaks $C(z, t)$ and the defining equation

$$\mu_1 = \frac{\displaystyle\int_0^\infty tC(z, t)dt}{\displaystyle\int_0^\infty C(z, t)dt}. \quad (5)$$

Since $C(z, t)$ occurs in both the numerator and denominator of Eq. (5), the detector used to measure the response peaks need not be calibrated to give concentrations. All that is necessary is that the signal be directly proportional to the concentration of tracer in the carrier stream. Then $C(z, t)$ can be replaced with the response signal itself.

Equation (4), with experimental values of μ_1 determined from Eq. (5), was used to evaluate adsorption equilibrium constants for the NO–Fe_2O_3 system.

EXPERIMENTAL

The apparatus consisted of a conventional gas chromatograph (with thermal conductivity detector) in which the separation column was replaced with a 0.54-cm-i.d. tube packed with Fe_2O_3-on-alumina particles. Care was taken to minimize the dead volumes between pulse injections and the entrance to the bed and between the exit of the bed and the detector. The total such volume was about 5 cm³. Helium (99.99%) carrier gas was further purified by passing through a bed of 13X molecular sieve particles maintained at liquid nitrogen temperature. Pulses consisting of 0.5-cm³ samples of 0.6% NO in helium were introduced to the bed by means of a seven-port sampling valve described by Schneider (8).

The Fe_2O_3/Al_2O_3 catalyst was prepared by first soaking spray-dried alumina particles in an aqueous solution of $Fe(NO_3)_3$ for 24 hr. The resulting slurry was dried for 24 hr at 100°C and then calcined in an air stream for 3 hr at 650°C. The material was crushed and sieved, retaining the fraction of 60–80 mesh for preparing the packed bed. The physical properties of the catalyst particles and of the bed are given in Table 1.

The runs with NO pulses were made by first pretreating the bed *in situ* with a stream of pure N_2O at 400°C for 1 hr in order to adsorb oxygen. Then a continuous stream of helium flowed through the bed, with NO pulses introduced at 30-min or 1-hr intervals. Data were obtained at temperatures from 370 to 410°C. As discussed later, during the time of helium flow, oxygen was desorbed from the Fe_2O_3 surface. Assuming that NO is adsorbed on the surface oxygen, the variation in retention time of the NO pulses with time of helium flow was a measure of extent of oxygen desorption. Three to five NO pulses were introduced in rapid succession at each time interval and the average of the first

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TABLE 1

Physical Properties of the Catalyst (Fe_2O_3/Al_2O_3) and the Bed and Operating Conditions

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Property	Method of measurement or calculation	Value
Wt% Fe_2O_3 on catalyst particles		14.2%
Surface area, S	Sorptmeter	35 m²/g
True density, ρ_t	Pycnometer	3.2 g/cm³
Apparent density, ρ_p	Mercury porosimeter (atmospheric pressure)	2.3 g/cm³
Porosity of particles, β	$\beta = 1 - (\rho_p/\rho_t)$	0.27
Pore volume, v_p	$(1/\rho_p) - (1/\rho_t)$	0.11 cm³/g
Average pore radius	$2v_p/S$	65 Å
Mesh range of particles		60 ~ 80 mesh
Average radius of particle, R		0.011 cm
Void fraction of bed, α		0.44
Length of packed bed		19 cm
i.d. of packed column		0.54 cm
Mass of Fe_2O_3 particles in bed		5.66 g
Pressure at exit of bed		1 atm
Pressure drop range		2.6–11 cm Hg

moments for each pulse was used for subsequent calculations. The moment values were obtained from the response curve and Eq. (5), using Simpson's rule for integration. At 400°C runs were made over a range of velocities (see Fig. 1) to verify the linear relation between the moments and z/v required by Eq. (4). Then for other temperatures the average moment for several pulses at a constant velocity corresponding to a gas flow rate of 50 cm³/min (at 25°C and 1 atm) was used. Other operating conditions are given in Table 1.

RESULTS AND DISCUSSION

Preliminary Experiments

Several types of *in situ* pretreatment of the catalyst bed were studied with the objective of obtaining reproducible results with various amounts of adsorbed oxygen. When hydrogen pretreatment was used, the NO reacted with the reduced surface at high temperatures to produce N_2. At lower temperatures the zeroth moment was less than unity, indicating irreversible adsorption. With helium pretreatment the first moment varied with time and was not reproducible. With oxygen pretreatment the first moment increased with time initially and then decreased at longer times, and reproducibility was again poor.

Since it has been found that N_2O reacts with the Fe_2O_3 surface to give atomically adsorbed oxygen (see Ref. (9) and Fig. 5), pretreatment with pure N_2O was attempted and found to give reproducible moments. The points in Fig. 1 for 400°C at the same helium flow times are a measure of this reproducibility. Also, after the N_2O pretreatment the zeroth moments of the NO pulses were unity, within experimental error, thus satisfying the requirement of reversible adsorption. As Fig. 1 shows, the first moment decreases with time of helium flow after pretreatment, suggesting that surface oxygen is being desorbed. This was verified by different measurements with pulses of N_2O, as described later. The reproducibility of $(\mu_1)_{NO}$ obtained after N_2O pretreatment indicated that a more stable and well-defined surface is obtained then with oxygen pretreatment. Perhaps this is expected in view of previous studies (10)
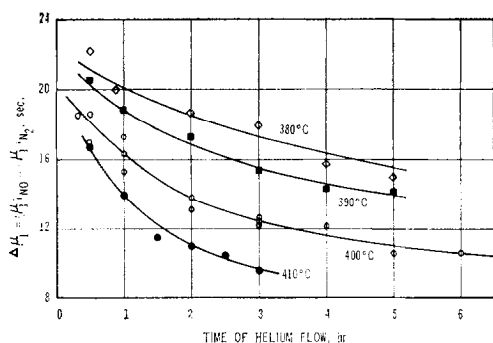
FIG. 1. Effect of time of helium flow on NO first moments in bed of Fe_2O_3/Al_2O_3 particles; helium flow rate = 50 cm³/min (at 25°C, 1 atm).

FIG. 2. Effect of NO concentration (in pulse) on first moment; temperature = 400°C; helium flow rate = 50 cm³/min (at 25°C, 1 atm).

showing that treatment of oxide surfaces with oxygen can give several types of surface species such as O_2, O_2^-, O^-, and O_3^-.

Chromatographic analysis of the effluent gas from the NO pulses introduced into the bed of particles showed no N_2 or NO_2, even at 410°C. Hence reaction to N_2 or NO_2 did not occur.

As a result of these preliminary experiments, the 1-hr pretreatment with pure N_2O at 400°C was adopted as a standard procedure. The moment results in Fig. 1 indicate that a quasi-stable surface was obtained after about 4 hr of helium flow. The moment data in this region at 400°C was used to test the applicability of Eq. (4). First, moments were measured in response to pulses containing from 0.3 to 1.0% NO. If the adsorption isotherm is linear, the first moment should be independent of NO concentration in the input pulse (8). The results shown in Fig. 2 suggest that the adsorption is linear up to about 0.6% so that an NO concentration in the pulse of this amount was allowable. Next, moments in the quasi-stable region were measured at 400°C over a range of velocities. These results, given in Fig. 3, show a reasonably well-defined straight-line relationship, as required by Eq. (1). The lower curve gives the first moments for nonadsorbed N_2 which were independent of temperature. The vertical
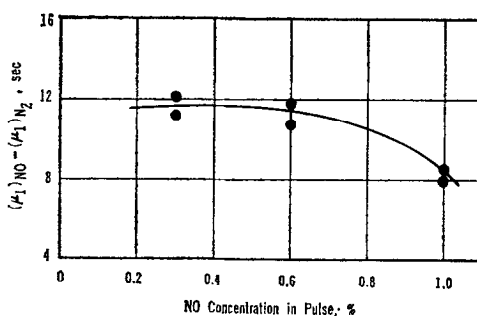
distance between the two curves is equal to $\Delta\mu_1$. In view of these tests, moment data at other temperatures were obtained at but one velocity, corresponding to a gas flow rate of 50 cm³/min (at 25°C and 1 atm), and the adsorption equilibrium constant calculated from Eq. (4).

Adsorption Equilibrium Constants

To attain the quasi-stable for measuring K_A for NO, the catalyst bed was maintained at 400°C with helium flow after the usual N_2O pretreatment. During this period, NO pulses were occasionally introduced to check the reproducibility of the response peaks. After 5 hr, reproducible
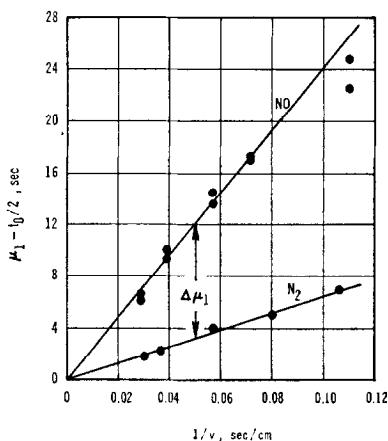

FIG. 3. Effect of gas velocity in bed on first moments of NO and N_2; temperature = 400°C and NO concentration in pulse = 0.6%.
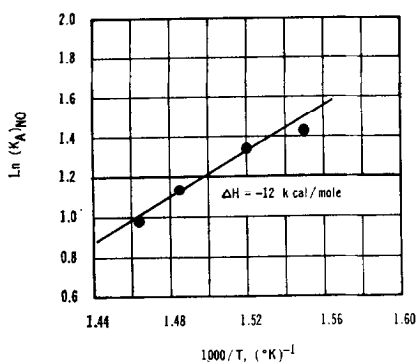
FIG. 4. Effect of temperature on adsorption equilibrium constant of NO.

peaks were obtained. Then the temperature of the bed was changed stepwise from 370 to 410°C, measuring first moments of the response peaks to NO pulses at each temperature level. The adsorption equilibrium constants calculated from Eq. (4) varied from 2.6 to 4.1 cm^3/(g of particles) and are plotted in Fig. 4 according to the van't Hoff equation. The slope of the line corresponds to a heat of adsorption of 12 kcal/mol. This is a reasonable magnitude for chemisorption but is considerably larger than 3 kcal/mol reported by Otto and Shelef (4) for NO on a supported Fe$_2$O$_3$ catalyst. However, their value was obtained, from gravimetric measurements of the amount of adsorption, at much lower temperatures (room temperature to 150°C) where nonactivated adsorption occurs. Also, the results given by our pulse experiments correspond essentially to zero surface coverage since the NO concentration in the pulse falls, near the entrance of the bed, from 0.6% to a very low value. The moment data shown in Fig. 1 at different temperatures, but prior to attaining the quasi-stable state, cannot be used to estimate the heat of adsorption, because the extent of surface oxygen varies with temperature as well as with time of helium flow.

Verification of Oxygen Desorption

When N$_2$O pulses are introduced into the bed the extent to which N$_2$, in the absence of oxygen, is found in the effluent peak is a measure of the oxygen adsorbed on the Fe$_2$O$_3$ particles. Such pulse tests with N$_2$O at 400°C were used to verify that the decrease in $(\mu_1)_{NO}$ with time of helium flow, as shown in Fig. 1, was due to a decrease in surface oxygen. The determination of N$_2$ and other gases was made by feeding the effluent peak from the bed of Fe$_2$O$_3$ particles into a normal gas chromatograph. A column of Porapak Q was used for separating N$_2$ + O$_2$ from N$_2$O and a 13X molecular sieve column for separating N$_2$ and O$_2$.

When N$_2$O pulses were introduced, in a helium stream, immediately after the standard treatment with N$_2$O, little nitrogen was produced. However, after 30 min or more of helium flow, considerable nitrogen was observed. This amount was obtained by adding the contributions from a series of pulses of N$_2$O introduced in rapid succession following a given period of helium flow. The results are shown in Fig. 5. Each point represents the total nitrogen determined by adding the contributions from all the pulses of N$_2$O introduced immediately after the indicated time of helium flow. The amount of nitrogen decreased in each successive pulse
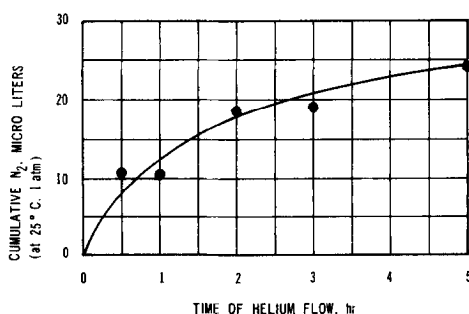

FIG. 5. Cumulative N$_2$ produced from N$_2$O pulses as a function of time of helium flow; temperature = 400°C; helium flow rate = 50 cm^3/min; and N$_2$O pulse volume = 0.5 cm^3.

of a series, reaching a constant small value. This constant, residual quantity seems likely to be due to the catalytic decomposition of N_2O into N_2 and O_2 on Fe_2O_3 and was neglected in calculating the nitrogen produced.

The amount of oxygen found in the effluent peaks during these experiments was less than 5% of the total N_2O decomposed, verifying that atomic oxygen was being added to the surface. Hence, the nitrogen produced as shown in Fig. 5 is a measure of the amount of atomic oxygen added to the Fe_2O_3 surface. The increase in nitrogen with time indicates that oxygen is slowly desorbed from the surface during the long periods of helium flow.

While the data points are scattered in Fig. 5, the reverse relationship between the curves in Figs. 1 and 5 is apparent. Figure 5 shows the oxygen deficiency of the Fe_2O_3 surface and how it increases with time, as measured by active sites for decomposition of N_2O to give atomic oxygen. The first moment data of Fig. 1 are a measure of the sites of atomically adsorbed oxygen upon which NO can be adsorbed. In principle, either type of data could be used to study the kinetics of desorption of oxygen from the surface of the Fe_2O_3/Al_2O_3 particles. We used the moment data because they are more accurate and were obtained over a range of temperatures.

Kinetics of Oxygen Desorption

The results just described for the N_2O pulse experiments are in agreement with the two-step scheme proposed by Winter (9) for the decomposition of N_2. In the first step N_2O is adsorbed on a site deficient in oxygen (indicated by the symbol $\sqcup$) yielding atomically adsorbed oxygen and nitrogen gas:

$$N_2O(g) + \sqcup \rightarrow N_2(g) + \lfloor O \rfloor. \qquad (6)$$
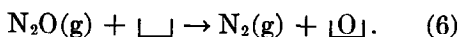
This is followed by the slow, rate-deter-

mining desorption of oxygen into the gas phase:

$$\sqcup 2 \rightarrow O_2(g) + \lfloor O \rfloor 2. \qquad (7)$$
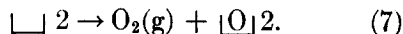
The slowness of the desorption step, as verified by the long time periods in Figs. 1 and 5, explains why oxygen was not detected in the helium stream from the bed of Fe_2O_3/Al_2O_3 particles. It seems likely that oxygen was slowly desorbing but the concentration in the helium stream was too low to measure. However, the NO moment data can be used as an alternate means of obtaining the kinetics of the second step. If the desorption is second order, following Eq. (7), the rate of change of θ, the fraction of the surface occupied by adsorbed oxygen, is

$$-d\theta/dt = k_2\theta^2 \qquad (8)$$

or, integrating,

$$1/\theta = k_2t + \text{constant}. \qquad (9)$$

Since θ is proportional to K_A and Eq. (4) states that K_A is proportional to $\Delta\mu_1$, Eq. (9) shows that $(\Delta\mu_1)^{-1}$ should be a linear function of time. The data in Fig. 1 are plotted in this way in Fig. 6. Reasonably good straight lines are obtained at each temperature level. A similar plot according to a first-order rate expression, that is, $\ln \theta$ vs t, showed a distinct deviation from linearity so that the second-order mechanism of Eq. (7) is more plausible.
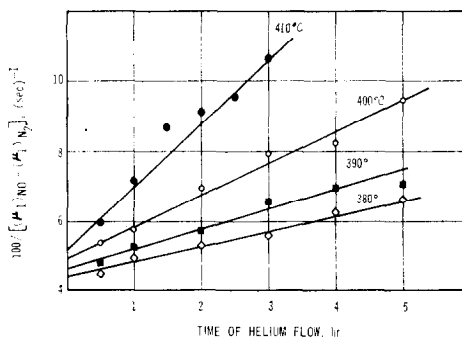

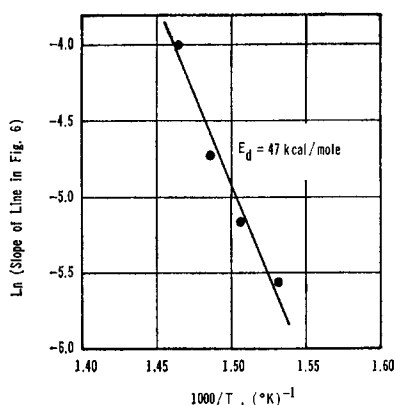FIG. 6. Second-order plot for kinetics of oxygen desorption from Fe_2O_3 surface.

The slopes of the lines in Fig. 6 are proportional to k_2. Hence, an Arrhenius-type graph of these slopes should give a straight line. The line drawn through the points in Fig. 7 corresponds to an activation energy E_d, for oxygen desorption of 47 kcal/mol. No published information was found for comparison with this result. The Fe–O bond energy is 33 kcal/mol. Hence, E_d, very approximately, would is expected to be between 33 and 66 kcal/mol, depending whether one or two Fe–O bonds

are broken in forming the activated complex for desorption.

In summary, our experimental results suggest that NO adsorption on Fe_2O_3 occurs on atomic oxygen adsorbed on the surface. Further, such oxygen appears to be slowly desorbed from the surface according to second-order kinetics and with a high activation energy.

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