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THE AUTHOR

V. W. Weekman, Jr. has been with Mobil Research and Development Corporation since his M.S. ChE at Michigan (1954), including a few years as a Mobil Fellow to obtain his Ph.D. in Chemical Engineering at Purdue (1963). He mentions his earlier career was tempered by the experience of operating laboratory pilot and bench scale units, followed by the chastening experience of interpreting kinetically such data, while in recent years he has had the thoroughly humbling experience of trying to explain commercial reactor behavior based on known and unknown principles. He is currently Manager of Systems Research. At other times he can be found sailing his ketch in the Chesapeake (with occasional Atlantic forays) with an enthusiasm which he ranks slightly below the level of irrational fanatic.

Iron Oxide Sorbents for Regenerative Sorption of NO_x

Supported ferric oxide can remove oxides of nitrogen from hot and cold gases, 20°C to 350°C, containing NO in the range of 50 to 1000 ppm when sufficient oxygen is present. Rates of sorption and capacities increase with oxygen concentration. The sorbent can be regenerated with air at 400° to 450°C an indefinite number of times.

Reduced iron oxide sorbs nitric oxide more rapidly than the ferric oxide and has a higher capacity. It can be regenerated with hot reducing gases.

LINUS LEUNG
and
DIMITRI GIDASPOW

Institute of Gas Technology
Chicago, Illinois 60616

SCOPE

Combustion of a fuel in air results in the formation of small but potentially harmful concentration of nitric oxide. To remove this air pollutant from flue gases and exhaust an effective sorbent is needed.

To estimate the size of potential sorbers from laboratory data it is desirable to obtain differential rate data. Such kinetic data are required for an estimate of the size of a rotary type sorber in which the sorbent is continuously regenerated (Gidaspow and Onischak, 1973). For the design of the more conventional fixed bed sorbers, capacity data is needed. Capacity data can be obtained from integrating the time dependent differential rate data.

Molecular sieves have been shown to have a high capacity for sorption of NO in the presence of oxygen (Joithe et al., 1972). However, due to interference by water vapor, they are not useful in treating flue gases and exhaust. The previously developed ferrous sulfate sorbent (Onischak and Gidaspow, 1973) is not useful at temperatures as high as 100°C or above and requires the use of an expensive catalyst for regeneration.

CONCLUSIONS AND SIGNIFICANCE

Exploratory data show that iron oxide sorbents have a potential application in treating flue gases and exhaust. They sorb NO_x at flue gas temperatures, at say 200° to 350°C. The ferric oxide sorbent can be regenerated with air at about 450°C. It sorbs NO in the presence of oxygen but unfortunately shows interference with water vapor. Water vapor does not interfere with the sorption of NO with the reduced oxide. The reduced sorbent is regenerated with 1% CO which is frequently present in the exhaust. The capacity of the reduced sorbent is a function of the method of preparation. Alumina coprecipitated with iron oxide gives an order of magnitude greater capacity than deposition of iron nitrate on porous alumina.

Differential rate and capacity data systematically obtained and correlated at 270°C for a supported ferric oxide powder allow a preliminary estimate to be made of the size of sorbers for a given duty. Breakthrough curves obtained for a reduced form of the iron oxide allow a limited scale-up of potential fixed bed sorbers.

Nitrogen oxides are produced whenever a fuel is burned in air. To remove this potentially toxic gas, scrubbing and catalytic conversion techniques are being developed (Lawrence, 1972). Most of the effort in connection with mobile sources such as automobiles has gone into the development of catalytic reactors (Koehl et al., 1971). To reduce nitrogen oxides into nitrogen and oxygen catalytically it appears that a reducing atmosphere is necessary (Patterson and Henein, 1972, p. 211). This requires operating the engine at less than optimum efficiency and conversion of the carbon monoxide thus inevitably produced in a second reactor into harmless carbon dioxide with addition of excess air. Figure 5.2 in Patterson and Henein shows that one pays a penalty of several miles per gallon in fuel economy by operating at less than optimum air-fuel ratio. Furthermore, catalysts intended to reduce the nitrogen oxide frequently produce ammonia instead (Meguerian and Lang, 1971). The ammonia produced in the first reactor will then burn in the second reactor giving back toxic nitrogen oxides. In addition, it has been demonstrated (Balgord, 1973) that catalysts containing nickel may produce air pollution by particles. Some combustion modifications for pollution control in stationary sources may also result in less than optimum fuel economy.

A method of removing oxides of nitrogen from mobile and stationary sources that does not have the above mentioned problems has been proposed by Gidaspow (1970). It involves sorbing oxides of nitrogen with a deposited chemical that can be regenerated, producing a highly concentrated mixture of nitrogen oxides. This concentrated gas is then returned to the source where it reacts with the fuel or is thermally decomposed. The object of this paper is to present inexpensive chemical compositions to make such schemes practical.

A number of sorbents had been previously proposed for removing nitric oxide from gases. Gidaspow and Onischak (1973) had successfully used ferrous sulfate mixed with silica gel. However, to prevent a slow aging of the sorbent by oxidation an expensive catalyst, platinum, was added to restore its activity with hot reducing gases. The gases had also to be cooled to near room temperature for best sorption. Molecular sieves (Brennan, 1962; Joithe et al., 1972; Sunderason et al., 1967) can sorb NO and can be regenerated. But they are known to sorb water preferentially to other gases and are therefore seriously considered only for applications such as nitric acid plants. The ferric oxide-sodium oxide sorbent (Ogg and Ray, 1954) proposed cannot work with multiple sorption and regeneration due to the conversion of the alkali oxide into a nitrate or carbonate that cannot be decomposed at reasonably low temperatures. Otto and Shelef (1970) experimented with a composition similar to the one under consideration for the purpose of possibly using iron oxides as catalysts for decomposition of nitric oxide. However, in their study of adsorption of pure nitric oxide they reported that the process is irreversible and spoke of inhibition by oxygen. We find that our ferric oxide sorbents can be thermally regenerated and do not sorb nitric oxide at high temperature (200°C and higher) unless oxygen is present in the gas stream. This was therefore an unexpected observation in view of the paper by Otto and Shelef. Closer to the observations of Otto and Shelef we do find that reduced iron oxide does sorb NO much better than the unreduced oxide except, of course, when we have high concentrations of oxygen in the gas. It is thus possible to remove NO_x from gases containing, say 2% oxygen and more as well as from reducing gases.

APPARATUS

The apparatus is similar to that in Gidaspow and Onischak's (1973) study. A significant addition is the use of an NO_x converter, manufactured by Thermo Electron. It converts all NO_x and ~80% of NH_3 in the stream into NO. The nitric oxide analyzer is LIRA-200, manufactured by Mine Safety Appliance. It analyzes NO in the ranges 0 to 1000 ppm and 0 to 2000 ppm.

A channel type sorber similar to the one used by Onischak and Gidaspow (1973) was built for this study to operate at high temperatures but was found inconvenient to use repeatedly due to problems with leaks. All data reported in this paper were obtained in a packed tube type reactor. It consisted of a quartz tube, 19 mm O.D., 16 mm I.D., and 0.47 m long. The sorbent was packed between two lumps of glass wool in the center of the tube. The length of the packing was about 25 mm.

SORBENTS

Three different sorbents, all iron oxides deposited on or coprecipitated with alumina, were tested. The first one, designated as FA, is a commercial hydrogenation catalyst (Fe-0303 *P*, supplied by Harshaw). It is Fe_2O_3 mounted on high activity alumina.

The second one, designated as FC, was prepared by impregnating an inert carrier (chromatographic alumina F-20, supplied by ALCOA) with an aqueous solution of ferric nitrate

Table 1. Physical Data for Ferric Oxide Sorbents

	FA	FC	FO
Iron content, wt. %	6.4	6.7	31.9
BET area fresh, m^2/g	138	178	37
Apparent bulk density, g/cm^3	1.09	0.85	1.42
Solid density, g/cm^3	3.44		4.18

Table 2. Typical Regeneration with a High Flow Rate of Nitrogen at 186° to 450°C

Time, min.	1	2	3	4	5	6	7	9	11	13
NO_x, ppm	45	15	75	445	665	310	95	172	38	10

Table 3. Rate of Regeneration with Nitrogen at Sorption Temperature

Temperature = 271°C

Time, min.	2	4	6	8	10
Rate (10^{-4} g NO/g sample-min)	1.25	0.37	0.2	0.14	10.1

and decomposing the nitrate at 500°C for 5 hours, similar to the preparation method used by Otto and Shelef (1970). The above procedure was repeated in order to deposit more iron on the alumina. The impregnated sorbent was sieved and only those particles that fell through a 100 mesh screen and were retained on a 150 mesh screen were used.

The third sorbent, designated as FO, was prepared by coprecipitation of ferric nitrate and aluminum nitrate (AVCO, 1969) as described in detail for sorption of SO_2. Physical data for the sorbents are given in Table 1.

EXPERIMENTAL PROCEDURE

The sorbent in the reactor was heated to the desired temperature for sorption. A dry $NO\text{-}N_2$ mixture from the cylinder was further mixed in the stream with dry air from another cylinder to give desired nitric oxide and oxygen concentrations. The mixed stream was monitored through the bypass and analyzed with the NO_x converter-Lira combination. At zero time, the mixed stream was switched to pass over the sorbent in the reactor and the outlet stream was continually analyzed for NO_x concentration until the sorbent was almost saturated.

For regeneration, pure nitrogen was passed over the sorbent while the sorbent was heated up rapidly to 450°C. The regeneration was deemed to be complete when no NO_x could be detected in the outlet stream from the reactor. The sorbent was then ready to sorb NO again. Typical regeneration data are given in Tables 2 and 3.

RATE DATA CALCULATION

Outlet concentration data from the Lira infrared analyzer are converted into rates of reaction by the following equation

$$\text{rate} = Q\, M_g (C_{\text{in}} - C_{\text{out}})/w \qquad (1)$$

Onischak and Gidaspow (1973) have already in great detail shown that for high enough flow rates, rates of reaction calculated using Equation (1) are differential reactor rates. Flow rate variation studies were also made for iron oxide studies by Leung (1973).

MATERIAL BALANCES

The material balances showing the amount of NO_x sorbed and the amount of NO_x regenerated are fairly good for sorption runs at 270°C or lower temperatures (Leung, 1973). However, at 350°C, the amount of NO_x regenerated was consistently less than the amount sorbed. Some of the NO_x could have decomposed catalytically at the high temperature.

For most regeneration runs, the total NO_x was measured by means of the NO_x converter and the Lira analyzer. In some runs, the NO_x converter was bypassed and it was found that more than 90% of NO_x regenerated was in the form of NO.

RATES OF SORPTION

For ferric oxide sorbents, the sorption of NO was not significant without the presence of oxygen. This is not surprising if a nitrate or nitrite is formed since both reactions require oxygen as a reactant. For all sorption runs, the rate of sorption dropped with time. At 270°C the rate of sorption drops exponentially for various NO and O_2 inlet concentrations at a constant temperature. Rate data for sorption of NO on sample FA are shown in Figures 1 and 2. The rate for each run can be correlated by means of the relation:

$$\text{rate} = \alpha e^{-\beta t} \qquad (2)$$

The dependence of α and β on NO concentration, at a fixed temperature, at 270°C, and at roughly the same concentration of oxygen, 2.8%, is shown in Figure 3. This initial rate α is first order with respect to NO concentration which is typical of many gas-solid reactions. The intrinsic rate β is also linear with respect to NO concentration but the intercept is significantly different from zero. The least square fitted equation is

$$\text{rate} = 0.713 \times 10^{-6} \cdot C_{NO} \cdot e^{-(0.285\times 10^{-3}\cdot C_{NO} + 0.149)t} \qquad (3)$$

The dependence of α and β on O_2 concentration at a fixed temperature and at roughly the same concentration of NO, 360 ppm, is shown in Figure 4. The intrinsic rate is linear with a nonzero intercept while the initial rate increases with oxygen concentration in a nonlinear manner.

The least square fitted equation is

$$\text{rate} = 1.53 \times 10^{-4} \cdot C_{O_2}{}^{0.56} \cdot e^{-(0.0327\cdot C_{O_2} + 0.153)t} \qquad (4)$$

Notice that the intercept constants, 0.149 from the variation of NO concentration data and 0.153 from the variation of O_2

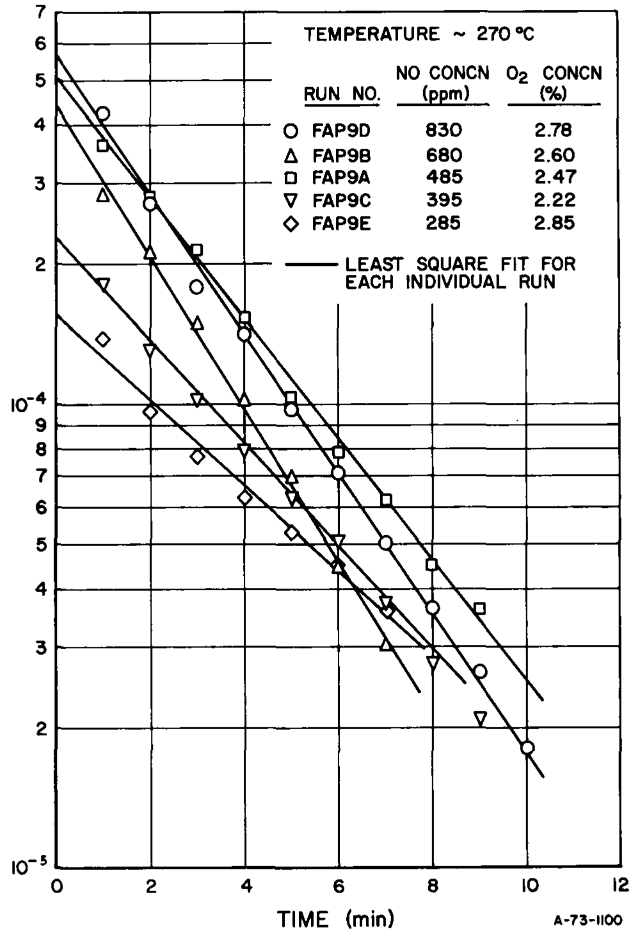

Fig. 1. Rate of sorption of nitric oxide on sample FA at various nitric oxide concentrations and approximately the same oxygen concentration (FA refers to sorbent FA and P refers to data taken in the packed tube).

concentration data, are not significantly different. This suggests that all the rate data can be correlated into a general form

$$\text{rate} = k_i C_{O_2}{}^n C_{NO}\, e^{-(kC_{O_2}\cdot C_{NO}+k')t} \tag{5}$$

The least square fitted values of the parameters are

	Constant	Standard deviation
k_i	$= 0.421 \times 10^{-6}$	0.350×10^{-7}
n	$= 0.561$	0.541×10^{-1}
k	$= 0.105 \times 10^{-3}$	0.197×10^{-4}
k'	$= 0.132$	0.413×10^{-1}

At lower temperatures the rate of sorption no longer follows an exponential relation. This made it impossible to evaluate activation energies and heats of reaction as was done with sorption of NO on nickel oxide (Cholera, 1973). In the nickel oxide study rates of reaction decreased exponentially with time at both room temperature and at 100°C.

At 195°C, rate data for sorption of NO on sample FC were correlated by a sum of two exponential terms. At an oxygen concentration of 3.5%, the rate equation was assumed to be of the form

$$\text{rate} = k_i C_{NO}\, e^{-kC_{NO}t} + \gamma\, C_{NO}\, e^{-\delta t} \tag{6}$$

The least square fitted values of the parameters turned out to be

	Constant	Standard deviation
k_1	$= 0.301 \times 10^{-6}$	0.298×10^{-7}
k	$= 0.709 \times 10^{-4}$	0.846×10^{-5}
γ	$= 0.767 \times 10^{-6}$	0.342×10^{-7}
δ	$= 1.085$	0.047

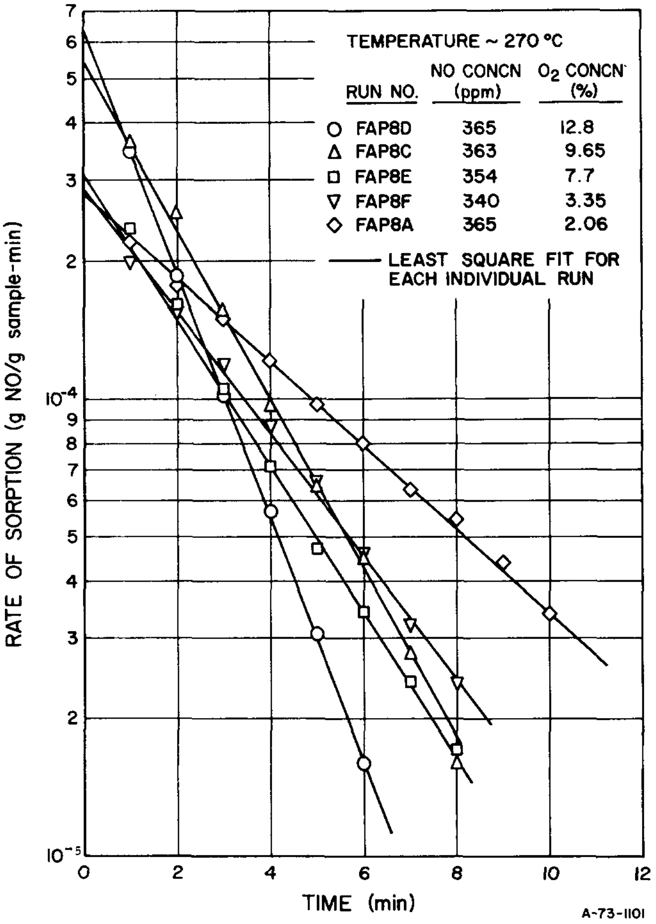

Fig. 2. Rate of sorption of nitric oxide on Sample FA at various oxygen concentrations and approximately the same nitric oxide concentration (FA refers to sorbent FA and P refers to data taken in the packed tube).

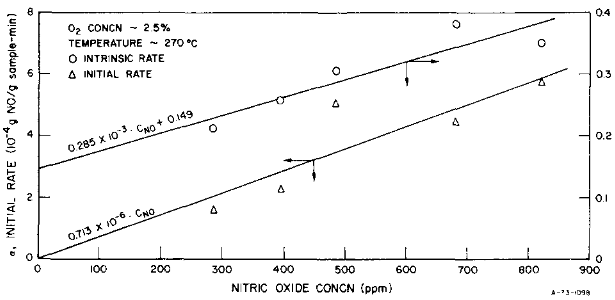

Fig. 3. Dependence of initial rate (α) and intrinsic rate (β) on nitric oxide concentration at a constant temperature and oxygen concentration.

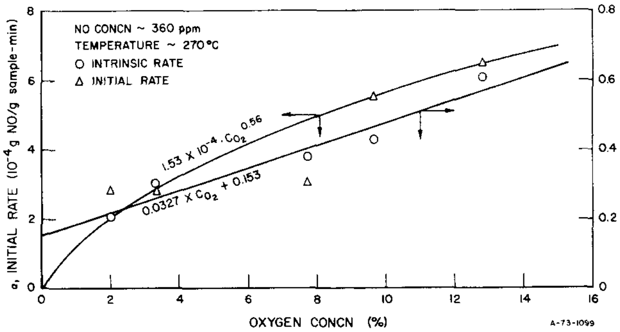

Fig. 4. Dependence of initial rate (α) and intrinsic rate (β) on oxygen concentration at constant temperature and nitric oxide concentration.

A plausible explanation for two exponential terms is that there are two parallel reactions at this temperature. The second reaction may be explained as physical sorption only (Leung, 1973).

MODEL

The correlation given by Equation (5) agrees with the theoretical prediction of the continuum model based on the concepts of first-order kinetics with respect to both gaseous and solid concentrations, diffusion into the sorbent, and pore closing. Gidaspow (1972) presented the original model for an irreversible reaction, and calculated effectiveness factors for a number of solid-gas reactions, such as the sorption of H_2S by CaO (Squires, et al., 1971). Similarly for a reversible gas-solid reaction of the type (Leung, 1973)

$$\gamma_A\, A(\text{gas}) + S(\text{solid}) \rightleftarrows \gamma\, P(\text{solid}) \tag{7}$$

a material balance for S, in this case ferric oxide, gives

$$\rho_S \frac{\partial \epsilon_S}{\partial t} = -\, r_v\, \epsilon_S + r_v{}'\, \epsilon_P\, M_S/\gamma\, M_P \tag{8}$$

Defining the solid concentrations as

$$C_i = \rho_i\, \epsilon_i \tag{9}$$

in more conventional terms Equation (8) can be written as

$$-\frac{dC_S}{dt} = k_A\, C_S\, C_A - k_A{}'\, C_P \tag{10}$$

Equation (10) also follows directly from the Law of Mass Action. The mass balance for the solid P gives the relation

$$C_P = (C_{P0} + \gamma\, C_{S0}) - C_S \tag{11}$$

Upon integration of Equation (10) and with the assumption of no solid product present at zero time, the rate of sorption of A, in this case nitric oxide, becomes

$$-\frac{dC_A}{dt} = -\gamma_A \frac{dC_S}{dt} = \gamma_A\, k_A\, C_A\, C_{S0}\, e^{-(k_A C_A + k_A'\gamma)t} \quad (12)$$

This is the expression for the rate when the solid reactant is completely accessible. When diffusion into the particle is important and the pores close due to a difference in the molar densities between the solid reactant and product, a diffusion equation with a chemical reaction has to be solved. Gidaspow (1972) and Leung (1973) found that for the case of ultimate incomplete solid reactant utilization, the rate of sorption of A is given by Equation (12) multiplied by an effectiveness factor, that is,

$$-\frac{dC_A}{dt} = \eta\, \gamma_A\, k_A\, C_A\, C_{S0}\, e^{-(k_A C_A + k_A'\gamma)t} \quad (13)$$

In Equation (13) η is the conventional effectiveness factor for catalytic reactions in a porous sphere (Satterfield and Sherwood, 1963). Now compare Equation (13) to the least square fitted Equation (5). From the exponential term we see that $k\, C_{O_2}$ is k_A, the forward rate constant, and k' is γ times k_A', the backward rate constant. The reason that the effect of oxygen concentration occurs in the rate constant is that its concentration is so much higher than that of NO and hence it behaves as a pseudo rate constant. In the initial rate, we see that $k_i\, C_{O_2}{}^n$ is $\eta\, \gamma_A\, k_A\, C_{S0}$.

Satterfield and Sherwood (1963) give the expression for η in terms of the Thiele modulus φ_s as

$$\eta = \frac{3}{\varphi_s}\left(\frac{1}{\tanh \varphi_s} - \frac{1}{\varphi_s}\right) \quad \varphi_s \quad (14)$$

The Thiele modulus is defined by

$$\varphi_s{}^2 = \frac{R^2\, k_v}{De} \quad (15)$$

In this case, the rate constant k_v is simply $k\, C_{O_2}$. When φ_s is large, we have the approximate relation

$$\left(\frac{1}{\tanh \varphi_s} - \frac{1}{\varphi_s}\right) \approx 1 \quad (16)$$

Therefore from Equation (14), we have

$$\eta \approx \frac{3}{\varphi_s} \quad (17)$$

This shows that η is proportional to $C_{O_2}{}^{-0.5}$.

Using this fact in Equation (13) we see that the initial rate should be proportional to $C_{O_2}{}^{0.5}$. Our data correlated by Equation (5) gave us $n = 0.56$, a value very close to the number 0.5 predicted theoretically.

We note that Uno et al. (1970) in their study of the reaction of SO_2 with MnO and O_2 reported a half order dependence of rate on oxygen concentration, but explained it by postulating a dissociation of oxygen.

CAPACITY FOR SORPTION OF NO

The total capacity for sample FA can be obtained by integrating the rate Equation (5) from $t = 0$ to $t = \infty$.

$$q = \int_0^\infty [0.421 \times 10^{-6} \cdot C_{O_2}{}^{0.56} \cdot C_{NO} \cdot e^{-(0.105 \times 10^{-3} \cdot C_{O_2} \cdot C_{NO} + 0.132)t}]\, dt$$

$$= \frac{0.421 \times 10^{-6} \cdot C_{O_2}{}^{0.56} \cdot C_{NO}}{0.105 \times 10^{3} \cdot C_{O_2} \cdot C_{NO} + 0.132} \quad (18)$$

Equation (18) resembles a Langmuir type isotherm. As an example, for $C_{O_2} = 2.78\%$ and $C_{NO} = 830$ ppm, we have

$$q = 1.64 \times 10^{-3} \text{ g NO/g sample} \quad (19)$$

If we assume that one mole of iron absorbs one mole of nitric oxide, knowing that our sorbent contains 6.5% iron by weight, the ideal total capacity becomes 0.0343 g NO/g sample. We then find that the total capacity from the rate data is only 4.78% of the stoichiometric capacity. The effectiveness factor may be attributed to the inaccessibility of most of the solid reactant. Our theory suggests that we look for better methods of preparing sorbents to make all of the iron oxide effective for reaction.

Breakthrough curves further illustrating the capacity of ferric oxide sorbents are given by Leung (1973). A quantitative relation between breakthrough curves and the differential rate data has been derived and discussed elsewhere (Leung and Gidaspow, 1973; Leung, 1973).

COMPARISON TO LITERATURE DATA

Otto and Shelef (1970) have obtained data for sorption of pure NO on ferric oxide. The capacity for sorbing NO for 6 to 24 hours for their sample at 150°C is estimated to be 1.05×10^{-3} g NO/g sample after extrapolating their data to 830 ppm NO concentration. Our data gave 1.64×10^{-3} g NO/g sample at 270°C in the presence of oxygen. This shows that our sorbent sorbs NO better, due to the presence of oxygen.

REDUCED IRON OXIDE

Otto and Shelef (1970) found that reduced iron oxide adsorbs pure NO better than the unreduced oxide. In order to improve the capacity and/or rate of NO sorption, we reduced our ferric oxide sorbent also. A typical run consisted of three parts:

1. Reduction with CO at about 450°C. The inlet concentration of CO was 1.6% and the flow rate was 1.6 lpm. The rate of CO consumption dropped as time went on. Reduction was stopped when the outlet concentration of CO reached 1.4%.
2. Sorption of NO at various conditions.
3. Thermal regeneration of the sorbent with nitrogen as already described for the ferric oxide.

After reduction, the sorbent was black in color. We found that the reduced iron oxide sorbed NO better than the unreduced iron oxide with respect to both rate and capacity. The reduced oxide sorbs NO with or without the presence of O_2.

Breakthrough Data

The degree of reduction indicated in the procedure was sufficient because further reduction did not improve the rate or the capacity for sorption of NO. For all runs with the reduced iron oxide without the presence of oxygen, the amount of NO_x regenerated was consistently much less than the amount sorbed. Probably, NO was reduced as well as sorbed by the reduced iron oxide. In the presence of oxygen material balances were again achieved. The rate of sorption of NO on reduced iron oxide without the presence of oxygen was so fast that our packed tube and parallel plate reactors were incapable of measuring differential rates of reaction. Reaction was over too quickly for small samples. Large samples used in the parallel plate reactor were in the diffusion controlled regime. Only breakthrough data could be obtained, such as those displayed in Figure 5. The graph shows that when outlet concentration is plotted versus the product of flow rate and time, all data at various flow rates fall on a single breakthrough curve. These facts indicate that the sorption is capacity limited.

For an infinitely fast irreversible reaction with no dispersion in the gas and solid phases a material balance gives the shock velocity

$$\text{shock velocity} = \frac{dx_A}{dt} = \frac{u\,M_S\,C_{in}}{\rho_S \gamma\,\epsilon_{S0}} \qquad (20)$$

where u is the superficial velocity of the gas through the bed and ϵ_{S0} is the initial fraction of solid reagent. In practice ϵ_{S0} may be the effective fraction of solid reagent. In Equation (19) it was assumed that only the solid stores mass, as is certainly true in the present situation. Amundson and co-workers (Leung and Gidaspow, 1973) had obtained similar expressions for shock velocity for the case of Langmuir type isotherms. M. N. Y. Lee (1972) shows how the shock velocity or the stoichiometric front velocity and the dispersion in Figure 5 which is related to the LUB concept (Leung and Gidaspow, 1973) can be used to design adsorbers. Our breakthrough data can be used similarly to design sorbers. The deviation of data from a perfect vertical line in Figure 5 cannot be quantitatively explained due to lack of rate data for the reduced iron oxide and analysis that couples our diffusion model to flow in the space between the particles.

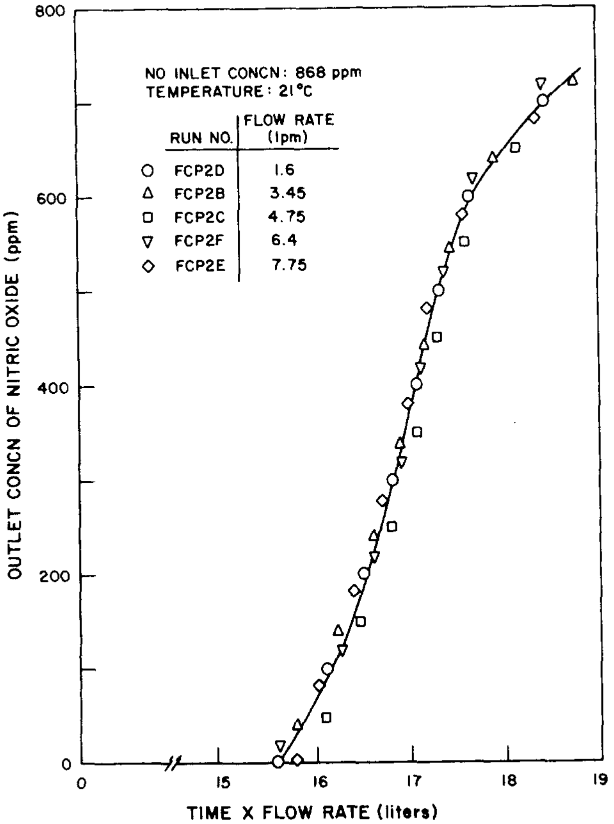

Fig. 5. The breakthrough curve generated by sorption of NO on reduced iron oxide at several flow rates.

Effect of O_2, CO_2, H_2O, and Method of Preparation

Table 4 gives the breakthrough data for sorption of NO on reduced iron oxides, showing the effect of O_2, CO_2, moisture, and preparation method.

The sorbent FO prepared by coprecipitation had the highest capacity but a somewhat lower rate as indicated by immediate breakthrough, followed by a slow rise in outlet concentration of NO_x. For the reduced iron oxide, FC, the presence of O_2 increases the capacity for sorption of NO. The rate, however, is somewhat lower because a smaller space velocity is required to reduce the NO concentration to zero in the exit stream. Also, the oxygen in the stream oxidized the reduced iron oxide back to the ferric oxide. Therefore reduction is necessary each time after regeneration.

Limited data in Table 4 indicate that the presence of CO_2 and a small amount of moisture did not decrease the sorption capacity of our reduced iron oxide sorbents. Moisture interference was found with the commercial ferric oxide sorbent, FA. It is, however, possible that some hydrates may be more effective sorbents, as is true in the case of sorption of H_2S with supported iron oxide (Gollmar et al., 1965) used in the gas industry.

COMPARISON OF DATA

After extrapolating the data of Otto and Shelf (1970) to 830 ppm. we found that their sorbent had a sorption capacity of 12 × 10^{-3} g NO/g sample for pure NO at 150°C. At 195°C our reduced sorbent had sorbed 3.47 × 10^{-3} g NO/g sample when C_{out} was 85% of C_{in}. The somewhat smaller quantity we obtain is not surprising since Otto and Shelef's sorption runs lasted as long as 24 hours as compared to 15 minutes for our runs.

The coprecipitated sorbent had a capacity of almost an order of magnitude higher. Note that its BET surface area is only one fifth that of the sorbent prepared by deposition. Such a lack of relation of BET surface area with capacity is consistent with the observations reported by the AVCO research group (AVCO, 1969) and others, and our interpretation of the mechanism of sorption. The final capacity, if made accessible by means of small iron oxide particle sizes and sufficiently large void volume, is measured by

Table 4. Breakthrough Data for Sorption of NO with Reduced Iron Oxide

Run no.	FCP 11	FCP 16A	FCP 16C	FO28	FO32
Temperature, °C	195	195	195	270	270
Flowrate, lpm	2.7	0.3	3.7	3.04	3.03
Wt. of sample, g	2.26	2.26	2.26	3.74	3.74
Space velocity, hr^{-1}	61,000	6,780	83,500	70,000	70,000
Nitric oxide conc., ppm	868	918	740	800	800
Oxygen conc., %	0	3.2	2.4	0	0
CO_2 conc., %	0	0	12.5	0	0
Moisture content, °F dewpoint	dry	dry	55	56	dry
Time to breakthrough, min	1.6	14	2	~0	~0
Capacity to breakthrough, 10^{-3} g NO/g sample	2.23	2.7	3.2	~0	~0
Capacity to $\frac{C_{out}}{C_{in}} = 0.85$ (10^{-3} g NO/g sample)	3.47	4.07	7.0	27.8	26.8

the amount of iron oxide used and not by the total BET area. The BET surface area number is only useful because it may measure the size of the iron oxide agglomerate that must be sufficiently small for the solid reagent to be accessible to the gas (Gidaspow, 1972). In this manner solid-gas reactions in which the solid is consumed differ from catalytic solid-gas reactions, where it is sometimes best to express rates based on BET area.

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NOTATION

A denotes gaseous pollutant to be sorbed
C_A = concentration of gaseous reactant A, moles/liter
C_{in} = inlet gaseous concentration, moles/liter
C_{NO} = nitric oxide concentration, ppm
C_{O_2} = oxygen concentration, mole %
C_{out} = outlet gaseous concentration, moles/liter
C_P = product concentration g/cm^3
C_{P0} = initial product concentration g/cm^3
C_S = solid concentration g/cm^3
C_{S0} = initial solid concentration g/cm^3
D_e = effective diffusivity within a particle, cm^2/s
k_A = forward rate constant defined by Equation (10)
k_A' = backward rate constant defined by Equation (10)
k = forward rate constant defined by Equation (5)
k' = backward rate constant defined by Equation (5)
k_i = initial rate constant, defined by Equation (5)
k_v = rate constant defined by Satterfield, corresponds to $k_A C_{O_2}$
M_g = molecular weight of gaseous reactant, g/mole
M_P = molecular weight of solid product, g/mole
M_S = molecular weight of solid reactant, g/mole
n = exponent of C_{O_2} in Equation (5)
P denotes product of reaction
Q = volumetric flow rate, lpm
q = total amount of gaseous reactant sorbed, g NO/g sample
R = radius of a particle
rate = rate of sorption, g NO/g-sample-min
r_v = forward rate per unit volume of solid reactant
r_v' = backward rate per unit volume of solid product
S = denotes solid reactant
t = time, min
u = apparent linear velocity, cm/s
w = weight of sorbent, g
x_A = spacial coordinate parallel to flow direction, cm

Greek Letters

α = initial rate g NO/g sample-min
β = intrinsic rate, min^{-1}
γ = parameter for data correlation, see Equation (6), also stoichiometric coefficient, see Equation (7)
γ_A = stoichiometric coefficient for reaction, see Equation (7)
δ = parameter for data correlation, see Equation (6)
ϵ_P = volume fraction of solid product
ϵ_S = volume fraction of solid reactant
ϵ_{S0} = initial volume fraction of solid reactant
η = conventional effectiveness factor
ρ_S = density of solid reactant, g/cm^3
φ_s = Thiele modulus, $(R^2 k_v/D_e)^{0.5}$

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