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Catalytic Reduction of Nitric Oxide with Various Hydrocarbons

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Conversion data for the reduction of nitric oxide with C_1 to C_8 hydrocarbons over a barium-promoted copper chromite catalyst were obtained in an integral flow reactor operated at atmospheric pressure and temperatures of 225° to 525°C. In general, an increase in carbon number in the hydrocarbon studied resulted in a decrease in the required temperature for a given nitric oxide conversion. For a given carbon number the required temperature for a given nitric oxide conversion decreased with degree of saturation. The data were fitted to empirical rate expressions.

Most recent research on prevention of air pollution by oxides of nitrogen has been devoted to the possibility of chemical destruction of air pollutants. Cohn and co-workers (*1*) reported in a U.S. patent the feasibility of a catalytic reactor to reduce nitrogen oxides by a suitable fuel and to oxidize the excess fuel. Baker and Doerr (*2*) demonstrated the application of a catalytic reactor for the reduction of nitrogen oxides by carbon monoxide in an automobile exhaust system.

Catalyst surveys for the oxidation of hydrocarbons have been performed by many authors (*3* to *7*). For the oxidation of methane, Anderson and co-workers (*5*) found that supported Cr_2O_3 was an effective catalyst. In a study of the light hydrocarbons (C_1-C_3), Accomazzo and Nobe (*3*) found that acetylene was more easily oxidized than methane over a copper oxide-alumina catalyst. By assuming first-order kinetics, Innes and Duffy observed that rate constants for carbon monoxide and hydrocarbon oxidation over vanadiaalumina catalysts increased with degree of unsaturation and molecular weight (*6*).

In contrast to the studies on oxidation of hydrocarbons and carbon monoxide, the work done on reduction of nitrogen oxides, particularly nitric oxide, has been mainly in the field of basic kinetics (*8* to *13*). Malling (*12*) found that over a zinc-promoted copper chromite catalyst methane reduced nitric oxide to nitrogen, carbon dioxide, and water. Ayen and Mahendroo (*8*) observed the same products for the reaction of ethane and nitric oxide over a barium-promoted copper chromite catalyst. The reaction of ethylene and nitric oxide has been found to produce essentially the same results (*13*).

The purpose of the work reported here was to study the effect of chain length, degree of saturation, and structure of various hydrocarbons on the rate of catalytic reduction of nitric oxide. The reaction

$$NO + \text{reducing agent} \rightarrow N_2 + CO_2 + H_2O$$

was studied in an isothermal integral reactor, with methane, ethane, ethylene, acetylene, propane, propylene, *n*-hexane, benzene, and *n*-octane used individually as reducing agents. At temperatures below 300°C. nitrous oxide, N_2O is formed in reactions of nitric oxide (*11, 14*).

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In order that the production of N_2O be kept to a minimum, reaction temperatures of 300°C. or higher were generally employed, with an extreme range of 225° to 525°C. Nitric oxide inlet concentrations were held at 10,000 p.p.m., or 1% by volume, while hydrocarbon concentrations were set at 10% in excess of the stoichiometric requirements for reduction to nitrogen, carbon dioxide, and water. The reverse reactions for the reduction of nitric oxide with hydrocarbons were neglected due to the large negative values for the standard free energy change for each reaction investigated (*15*).

EXPERIMENTAL APPARATUS

Reactor and Flow System

The experimental results were obtained from a type 304 stainless steel flow reactor operated isothermally and at atmospheric pressure. The reactor was 40 in. long with an I.D. of 1.049 in. The catalyst zone, about 15 in. deep, started approximately 14 in. from the exit of the reactor. Eight iron-constantan thermocouples were installed 1.75 in. apart in the reaction zone. For most of the work reported, a catalyst bed depth of 2.5 in. was used, with two of the thermocouples located within the catalyst bed. A Leeds and Northrup millivolt potentiometer was used to measure temperatures. In addition, one of the thermocouples placed within the catalyst bed was connected to a Sim-Ply-Trol temperature controller and indicator manufactured by Assembly Products Incorporated. The reactor was electrically heated with embedded nichrome wire. Two heating elements were controlled manually by variable autotransformers. A third heating element covered the reaction bed itself and was connected to the temperature controller. Temperatures in the catalyst bed were controlled to within ± 2°C. of the desired level.

The gaseous components of the feed stream to the reactor—NO, CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_8, C_3H_6, and He—were fed from pressurized tanks through pressure reducers, needle valves, and calibrated capillary tube flowmeters for flow rate measurement. Benzene, *n*-hexane, and *n*-octane are liquids at room temperature and atmospheric pressure. To feed these reducing agents to the reactor at accurately known low liquid-flow rates, a syringe pump was designed and constructed. The syringe pump had a maximum capacity of one 100-cc. syringe. The minimum capacity was determined by the smallest available syringe. For the data presented here, a reproducible liquid flow rate of 0.01045 cc./min. was used.

Figure 1 shows schematically the flow system employed. Wherever possible in the system, stainless steel type 316 Swagelok fittings and tubing were installed. Glass and Tygon tubing were used in the construction of the flow monometers. A stainless steel pipe, 1.05 in. O.D., filled with glass beads and equipped with threaded end-caps, was used to premix the feed stream to the reactor. Sample points before and after the reactor were also built into the flow system.

Due to the high vapor pressures of benzene, *h*-hexane, and *n*-octane, it was possible to evaporate the liquid components of the feed stream as they were fed to the reactor system. A large helium flow rate was directed to the syringe pump by closing valves four and six while five and seven were opened. Helium passed concentrically along a 6-in. long, 20-gauge syringe needle which was enclosed by ⅛-in. stainless steel tubing. As the syringe pump injected the liquid hydrocarbons into the closed system, the helium was observed to evaporate the liquid droplets completely at a steady rate. Pressure variations in the flow system were not observed and, in general, no complications were encountered with the liquids fed in this manner. The syringe pump as designed and operated proved to be an efficient and simple way of feeding liquids at low flow rates (*15*).

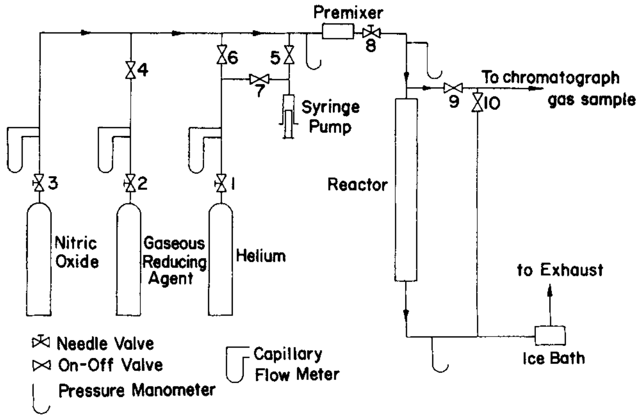

Fig. 1. Schematic diagram of reactor flow system.

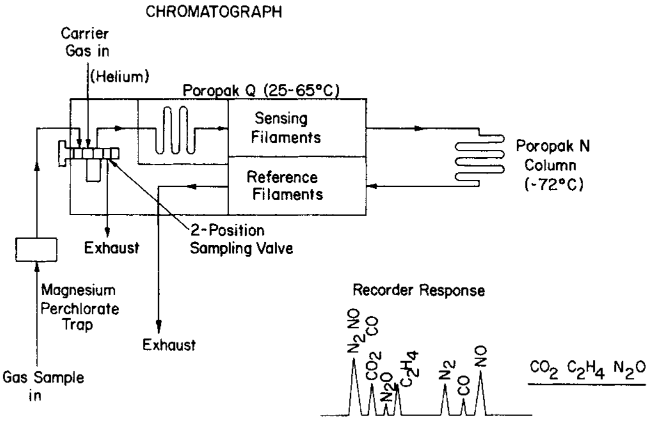

Fig. 2. Modifications to gas chromatograph and typical component separation.

Analytical Equipment

Gas streams entering and leaving the reactor were analyzed with a model 90P3 Aerograph gas chromatograph with a thermal conductivity detector. The response from the chromatograph was fed to a Sargent Model SR Recorder with a Disc integrator. In order to obtain separate peaks for N_2O, CO_2, N_2, CO, NO, and the particular hydrocarbon under investigation, a dual-column system was used. Figure 2 is a schematic diagram of the gas chromatograph system.

The gas sample was passed through a magnesium perchlorate trap for the removal of water. Periodically this trap was removed from the system to determine the extent of adsorption of the other gaseous components present in the sample. These tests showed no evidence of CO, CO_2, N_2, N_2O, or NO adsorption. Benzene, *n*-hexane, and *n*-octane were the only reducing agents which appeared to be adsorbed by the magnesium perchlorate.

Table 1[*] lists the retention times of various components separated in the Porapak Q column.[*] Separation of NO, CO, and N_2 was obtained in a stainless steel column packed with Porapak N, and maintained at —72°C. Benzene, *n*-hexane, and *n*-octane were condensed from the gas sample in an ice bath. Concentrations in the gas sample of less than 50 p.p.m. could not be detected by the analytical system used in this study. Additional details of the analytical system are available (*15*).

Calibration of Gas Chromatograph

With the arrangement of the Porapak columns shown in Figure 2, it was possible to obtain separate peaks for nitrogen, nitric oxide, carbon monoxide, carbon dioxide, nitrous oxide, methane, ethylene, acetylene, ethane, propylene, and

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[*] Table 1 has been deposited as document 01321 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 W. 34th St., New York 10001 and may be obtained for $2.00 for microfiche or $6.50 for photocopies.

propane. Analyses for water, benzene, *n*-hexane, and *n*-octane were not possible because they were permanently absorbed by the Porapak N column at −72°C. Approximately every 12 hr. the Porapak N column was placed in a hot water bath and purged. This procedure removed the adsorbed components from the column.

By employing the calibrated flow manometers, known mixtures of nitric oxide and the various hydrocarbons investigated were passed through the gas chromatograph. The gas chromatograph was also calibrated for known mixtures of CO_2, N_2, and N_2O. In terms of peak area units, responses from the chromatograph for the various components were found to be directly proportional to concentration over the range of interest. The carbon dioxide, nitrous oxide, and reducing agent peaks were measured after the gas sample had passed through the Porapak Q column. The peaks for nitric oxide, nitrogen, and carbon monoxide were measured after the gas sample had left the Porapak N column.

After about three quarters of the experiments were finished, the Porapak N column failed. A molecular sieve 5A column was found to be a suitable replacement, in agreement with the experience of Malling (*12*).

Ayen and Mahendroo (*8*), Nobe and Sotoodehia (*13*), and Malling (*12*) have reported that the chief reaction products of the reactions of NO with CH_4, C_2H_6, and C_2H_4 were essentially CO_2, N_2, and H_2O. Baker and Doerr (*11*) and Shelef and Otto (*14*) have reported N_2O formation by the NO-CO reaction. In this study N_2O formation was generally negligible, with less than 50 p.p.m. in the product stream. On the basis of previous work, it was suspected that only N_2, CO_2, and H_2O would be observed as products. Ammonia production has been found in the reduction of NO with hydrogen (*10*). By analyzing the magnesium perchlorate trap, no traces of ammonia could be detected. In all the reactions investigated, the number of moles of nitric oxide that reacted were essentially equal, stoichiometrically, to the number of moles of the reducing agent that reacted. Periodic material balances confirmed the assumption that the only reaction products were CO_2, N_2, H_2O, and under certain circumstances which will be discussed later, CO and N_2O.

Samples of both the reactant stream and product stream were fed to the gas chromatograph for analysis. The fractional conversion of nitric oxide in the reactor was set equal to the fractional decrease in the peak area. Except for benzene, *n*-hexane, and *n*-octane, the same procedure was applied to the reducing agents investigated in order to determine their extent of reaction. The assumption of negligible volume change with reaction was valid because the helium concentration in the reactor was approximately 99% by volume at all times and the maximum change in the number of moles for a given reaction was two. The maximum increase in total volume was 0.13%. The integrator on the recorder could be read to within ± 5 area units. This corresponded to a 0.4% error in the NO concentration recording and approximately a 1% error in the hydrocarbon concentration recording.

EXPERIMENTAL PROCEDURE

Two types of catalysts, furnished by Girdler Catalysts and recommended for the reduction of nitric oxide, were tried in the reactor. Girdler G-43, platinum on alumina, gave appreciable reduction of NO with methane and ethylene only at reaction temperatures above 400°C. It was also found that temperature control of the catalyst was a problem with this catalyst. Since most of the literature devoted to the reduction of nitric oxide is concerned chiefly with copper-containing catalysts (*2*, *8* to *12*, *16*), Girdler G-22, barium-promoted copper chromite, was selected for further studies. Physical properties of this catalyst have been reported previously (*9*). Preliminary investigations with methane and ethylene as reducing agents revealed that appreciable NO conversions were possible between 300° and 500°C. This confirmed results reported in the literature for similar catalysts (*12*, *13*).

The importance of extraneous effects was determined before the experimental data were taken. With ethylene as the reducing agent, several runs were performed with no catalyst in the reactor at 300°, 400°, and 600°C. to determine what effect the reactor had on the reduction of nitric oxide. No reaction products were detected. In studies using methane (*12*) and ethane (*8*) as the reducing agents, the same results were observed for other empty stainless steel reactors.

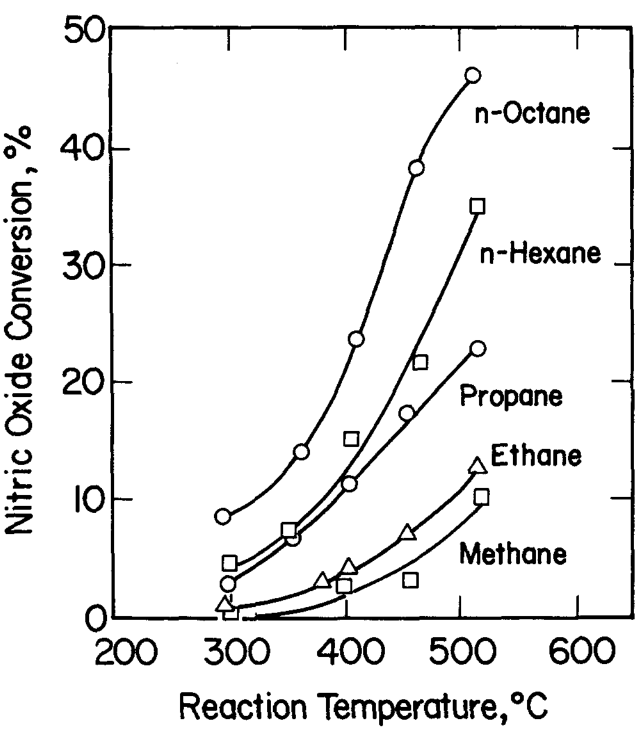

Fig. 3. The effect of carbon number on reduction of nitric oxide by saturated hydrocarbons.

According to Equation (1), for constant W/F_{NO} ratios, initial feed conditions, reaction temperatures, and assuming plug flow, the conversion (X_{NO}) should remain constant if the reaction rate is independent of gas-film resistance (*14*).

$$\frac{W}{F_{NO}} = \int_0^{X_{NO}} \frac{dX_{NO}}{r_{NO}} \tag{1}$$

To determine the effect of bulk gas diffusion, the ratio W/F_{NO} was held constant at 6.05×10^3 (g.-catalyst)(min.)/g.-mole NO, while the weight of catalyst was varied from 1.56 to 8.72 g. With ethylene as the reducing agent, it was observed that NO conversions remained constant at total gas flow rates above 2,400 cc./min. measured at standard temperature and pressure. Flow rates of 3,100, 3,240, and 3,580 cc./min. were used for all subsequent work.

Pore-diffusion effects were not studied. Several authors have reported that reducing the size of the Girdler G-22 catalyst pellets has no effect upon the reduction of nitric oxide with carbon monoxide (*9*) and ethane (*8*). Sample calculations were performed for each NO-hydrocarbon reaction investigated, in order to determine the effect of catalyst pellet size on the Thiele parameter. Within reasonable approximations, the calculations (*15*) revealed that pore-diffusion resistance was a factor only at reaction temperatures above 500°C.

The reactor was loaded with 8.72 g. of Girdler G-22 catalyst (3/16 in. × 1/8 in. tablets) and diluted with stainless steel particles. Preliminary experiments with a 7-in. deep catalyst bed indicated that logarithmic loading of the catalyst minimized the axial temperature gradient. In using this technique, most of the catalyst was loaded at the top of the reactor bed. The heat release rate due to the reaction is an exponential function of temperature and this loading method distributed this heat throughout the catalyst bed.

Previous investigations (*9*, *16*) have shown that Girdler's G-22 catalyst can exist in a reduced or oxidized state. For the work reported here, the catalyst was initially prereduced by passing H_2 gas over it for 24 hr. at 300°C. A 3-hr. period of H_2 reduction at 300°C. was employed after each NO-hydrocarbon reaction was studied. A standard run at 300°C. of 10,000 p.p.m. NO, 1,840 p.p.m. C_2H_4, and 3,280 cc./min. total gas flow (measured at standard temperature and pressure) was performed before and after each series of hydrocarbon runs. This standard run made it possible to determine the catalyst activity throughout the experiment.

After the catalyst was loaded in the reactor, the standard run was performed three times a day for approximately 1,437 hr. The catalyst activity appeared to stabilize, and an activity of 1.0 was assigned to run 2. The activity was observed to return approximately to the original value when the catalyst was subjected to the 3-hr. H_2 treatment after each series of hydrocarbon runs. For the NO-C_2H_2 reaction the catalyst activity dropped by 37% between hydrogen treatments. Over the entire period of operation (2,192 hr.) the activity of the catalyst when freshly treated with hydrogen was observed to decrease by 20%. The one charge of catalyst was left in the reactor throughout the entire study. During shutdowns, helium flow was maintained through the reactor. After each hydrogen reduction process a flow of 200 to 400 cc./min. of helium was used to purge the reactor for a 12-hr. period.

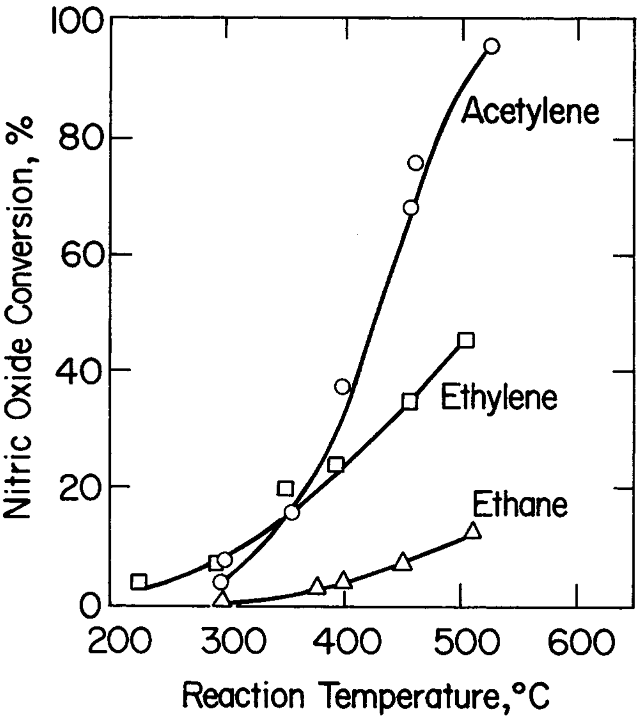

Fig. 4. The effect of hydrocarbon saturation on nitric oxide reduction by C_2 compounds.

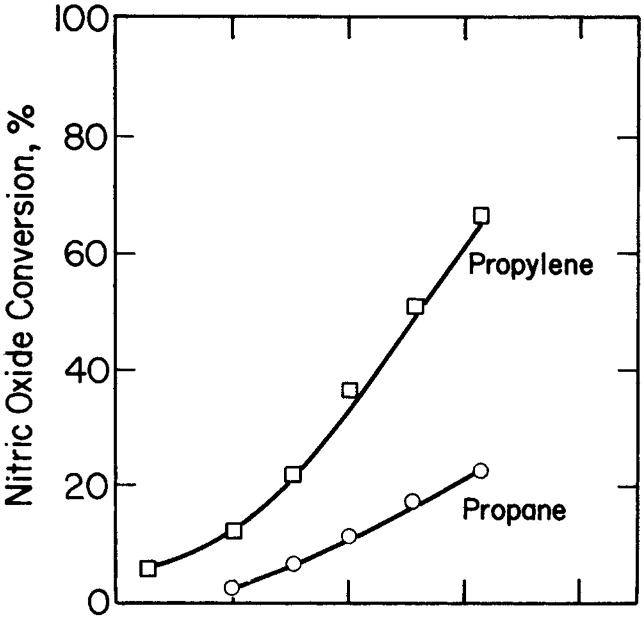

Fig. 5. The effect of hydrocarbon saturation on nitric oxide reduction by C_3 compounds.

TABLE 2. EXPERIMENTAL CONDITIONS USED FOR HYDROCARBON COMPARISONS (FIGURES 3 THROUGH 6)

Hydrocarbon	Inlet partial pressure, atm.	Total molar flow rate, g.-moles/min.
Methane	0.00275	0.145
Acetylene	0.0022	0.145
Ethylene	0.00184	0.145
Ethane	0.00158	0.145
Propylene	0.00122	0.145
Propane	0.0011	0.145
Benzene	0.00073	0.160
n-Hexane	0.00058	0.139
n-Octane	0.00044	0.160

NO inlet partial pressure for all runs: 0.01 atm. Catalyst weight: 8.72 g.

TABLE 3. CATALYST DEACTIVATION RATES FOR BARIUM-PROMOTED COPPER CHROMITE

Weight of catalyst: 8.72 g.

Reducing agent	Deactivation rate,* % decrease/100 hr.
Methane, CH_4	0.36
Ethylene, C_2H_4	3.62
Ethane, C_2H_6	3.90
Propylene, C_3H_6	4.45
n-Octane, C_8H_{18}	4.53
Benzene, C_6H_6	6.40
n-Hexane, C_6H_{14}	10.30
Propane, C_3H_8	11.30
Acetylene, C_2H_2	18.30
Overall catalyst deactivation rate	0.91

* Based on nitric oxide conversion measured for a standard run of 10,000 p.p.m. NO and 1,840 p.p.m. C_2H_4 at 300°C. reaction temperature and 0.145 g.-moles total gas flow per minute.

EXPERIMENTAL RESULTS

For the NO-hydrocarbon reactions investigated, the observable products were chiefly CO_2, N_2, and H_2O. At temperatures below 300°C., small traces of N_2O were detected. These results confirm the conclusions of other investigators (*8*, *9*, *11* to *14*) for the reactions of nitric oxide with carbon monoxide, methane, ethane, and ethylene.

Results from the hydrocarbon comparison runs, in the form of plots of nitric oxide conversion versus temperature, are presented in Figures 3 through 6. These data have been corrected for variations in catalyst activity. Inlet nitric oxide and hydrocarbon concentrations were, respectively, 10,000 p.p.m. and 10% in excess of the stoichiometric requirements for reduction to N_2, CO_2, and H_2O. The formation of CO and N_2O was negligibly small at all times. Carbon monoxide formation was never observed with the barium-promoted copper chromite catalyst. Feeds were therefore based on CO_2, N_2, and H_2O as products. Actual hydrocarbon concentrations and total molar flow rates are presented in Table 2.

Figure 3 presents the data for the catalytic reduction of nitric oxide with the saturated hydrocarbons (C_1-C_8). The data for the reduction of nitric oxide with the unsaturated hydrocarbons (C_2-C_3) are shown in Figures 4 and 5. Figure 6 compares the reactivity of two C_6 compounds of different structure, *n*-hexane and benzene. The experimental data presented in Figures 3 to 6 were correlated with an empirical rate expression by an integral analysis to be described later.

Runs with varying inlet partial pressures were performed only for the NO-hexane reaction. Figure 7 shows the effect of varying NO partial pressures from 0.01 to 0.00686 atm. and *n*-hexane partial pressures from 0.00056 to 0.000496 atm. With *n*-hexane fed to the reactor in 58% excess of the stoichiometric requirements, nitric oxide reduction was observed to be approximately twice that measured at 10% excess of *n*-hexane.

Table 3 reports a catalyst deactivation rate, expressed as percent decrease per 100 hr. of operation, for each NO-hydrocarbon reaction investigated. A comparison of the various reducing agents' catalyst deactivation rates revealed that the NO-C_2H_2 reaction produced the largest decrease in catalyst activity. In general catalyst activity deactivation rates were higher for the saturated hydrocarbons than for unsaturated hydrocarbons of the same carbon number. An overall catalyst deactivation rate of 0.91% decrease per 100 hr. was observed. The low number can be attributed to the fact that the catalyst was reduced with hydrogen after each series of hydrocarbon runs.

A preliminary investigation using a platinum-on-alumina catalyst (Girdler G-43 as 0.25-in. by 0.25 in. tablets) indicated that methane is a more efficient reducing agent for nitric oxide than is ethylene (see Table 4). Similar investigations on a barium-promoted copper chromite catalyst (Girdler G-22) revealed that ethylene reduced nitric oxide more rapidly than did methane. Carbon monoxide production was observed when ethylene was used to reduce nitric oxide over the platinum-on-alumina catalyst. In the NO-hydrocarbon reactions investigations over the barium-promoted copper chromite catalyst, carbon monoxide production was not detected.

INTERPRETATION AND DISCUSSION OF RESULTS

Several generalizations can be made after inspections of Figures 3 through 6. An increase in carbon number decreased the temperature required for a given conversion for the reduction of nitric oxide with hydrocarbons. For a given carbon number, the required temperature decreased with degree of saturation. Accomazzo and Nobe (3) and Innes and Duffy (6) observed the same effect of hydrocarbon structure on the oxidation of hydrocarbons with air over copper oxide-alumina and vanadia-alumina catalysts, respectively. Although inlet feed concentrations were not varied in the work leading to the above conclusions, reactant partial pressure should have only a minor effect on orders of reactivity. As will be pointed out later, reaction orders were approximately the same for all hydrocarbons studied.

Andersen, Green, and Steele (*17*) observed that the carbon-containing reducing agents form some carbon monoxide in the reduction of nitric oxide over precious metal catalysts. High fuel excess increased the amount of carbon monoxide formed. In a preliminary investigation over a platinum-on-alumina catalyst (see Table 4), it was found that the NO-ethylene reaction produced small amounts of carbon monoxide. The NO-methane reaction was observed to produce no carbon monoxide. The reducing agents (CH_4 and C_2H_4) were fed to the reactor in 10% excess of the stoichiometric requirements of this study. Carbon monoxide production was detected in previous investigations (*17*) only when large excesses of the reducing agent were used.

Also observed in the investigation with the platinum-on-alumina catalyst was that the NO-methane reaction at

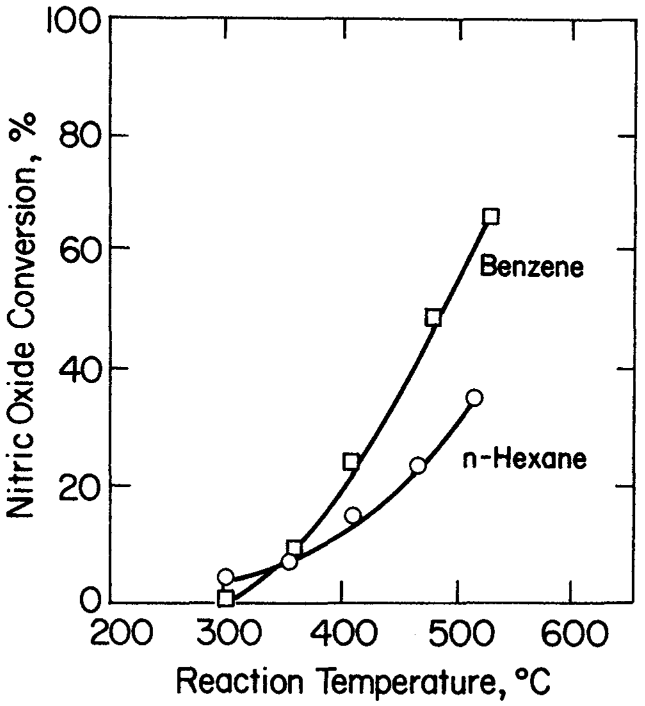

Fig. 6. The effect of hydrocarbon structure on nitric oxide reduction by benzene and *n*-hexane.

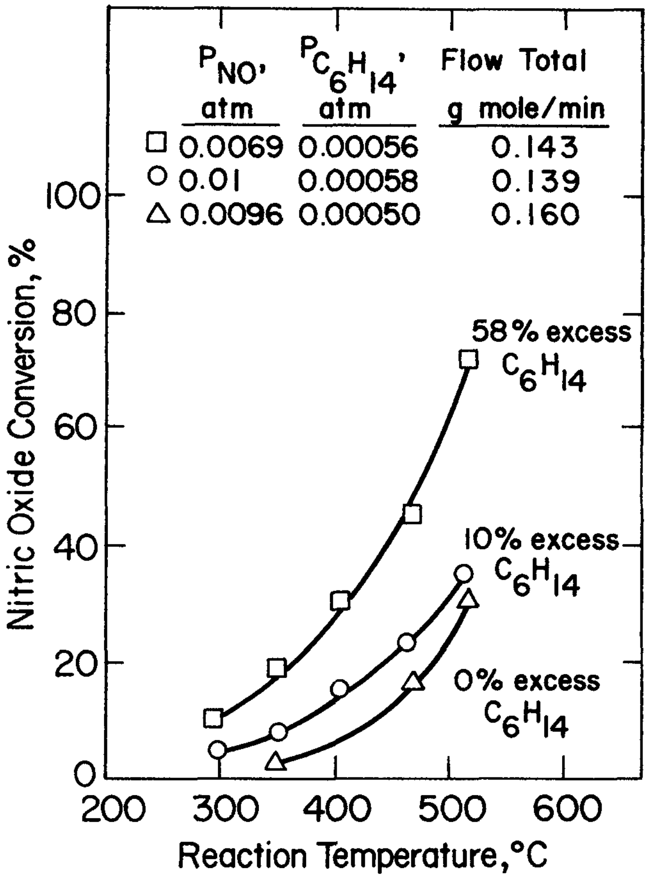

Fig. 7. The effect of feed stoichiometry on nitric oxide reduction by *n*-hexane.

a given temperature gave a higher nitric oxide conversion than the NO-ethylene reaction. As shown in Figure 8, an opposite order of reactivity was observed over the barium-promoted copper chromite catalyst.

The same barium-promoted copper catalyst was used for 3,629 hr. The activity (based upon a standard run) was observed to drop by 40% over this time period. During the period in which the experimental data were taken (2,192 hr.), the catalyst activity decreased by 20%. It was found that different NO-hydrocarbon reactions caused the catalyst activity to fall at different rates. The activity was observed to decrease by 32% for the NO-acetylene reaction over a 212-hr. period as compared to no apparent decline in catalyst activity for the NO-methane reaction over a 278-hr. period. Complete information on catalyst deactivation is available elsewhere (*15*).

Accomazzo and Nobe (*3*) found that CO_2 and H_2O present in the feed stream tended to decrease the activity of a copper oxide-alumina catalyst used for the oxidation of hydrocarbons with air. This decrease in activity was observed to be reversible in nature. Heating the catalyst to remove the adsorbed CO_2 and H_2O returned the activity to its original activity (*3*). Since high nitric oxide conversions (96%) were observed for some of the NO-hydrocarbons studied, it might be concluded that the amounts of CO_2 and H_2O produced by the various reactions resulted in the difference in the catalyst deactivation rates observed (see Table 3). This conclusion is supported by the observation that catalyst activity was increased slightly after each helium flow period. However, complete catalyst activity was not restored until the catalyst was treated with H_2. This indicates that deactivation was due to both adsorption and oxidation effects.

TABLE 4. NITRIC OXIDE REDUCTION WITH METHANE AND ETHYLENE OVER A PLATINUM-ON-ALUMINA CATALYST (GIRDLER G-43)

Weight of catalyst: 10.2 g.

Total gas flow, g. moles/min.	P_{NOi}	P_{HCi}	Temp., °C.	NO Conversion fraction
Ethylene				
0.102	0.0119	0.00277	345	0.00
0.107	0.0128	0.00298	370	0.03
0.100	0.0136	0.00165	402	0.16
0.102	0.0239	0.00340	540	0.40
Methane				
0.102	0.0142	0.00370	350	0.06
0.127	0.0090	0.00251	428	0.73
0.127	0.0090	0.00251	436	0.76
0.102	0.0270	0.00605	567	0.86
0.102	0.0142	0.00370	607	0.83

TABLE 5. EMPIRICAL RATE EXPRESSIONS FOR THE CATALYTIC REDUCTION OF NITRIC OXIDE

$r_{NO} = Ae^{-E/(RT)} P_{HC}^{0.5} P_{NO}^{0.5}$ g.-moles NO converted/(g.catalyst)(min.)

Reducing agent	A, g.-moles NO converted / (g.-catalyst)(min.)(atm.)	E, cal./g.-mole	S, standard deviation of r_{NO}
Methane, CH_4	11.8	12,850	0.0107
Ethane, C_2H_6	7.12	11,080	0.0022
Ethylene, C_2H_4	3.94	8,000	0.0214
Acetylene, C_2H_2	1,104	14,700	0.0326
Propane, C_3H_8	4.48	8,930	0.0133
Propylene, C_3H_6	12.9	8,600	0.0188
n-Hexane, C_6H_{14}	11.6	9,400	0.0109
Benzene, C_6H_6	292	13,000	0.0295
n-Octane, C_8H_{18}	9.80	8,000	0.0242
Carbon monoxide, CO (ref. *9*)	0.50	4,830	0.0195
Methane, CH_4 (ref. *12*)	11.1	12,500	0.0200
Ethane, C_2H_6 (Ref. *8*)	547	14,800	0.0398

Rate Expressions

Order-type rate expressions of the form

$$r = Ae^{-E/RT} P^{\alpha}_{HC} P^{\beta}_{NO} \qquad (2)$$

were used in developing rate expressions. For an isothermal integral flow reactor, the design equation for this study was

$$\left(\frac{W}{F_{NO}}\right) (Ae^{-E/(RT)}) (P^{\alpha}_{HCi} P^{\beta}_{NOi}) = \int_0^{X_{NO}} \frac{dX_{NO}}{\left(1 - \frac{X_{NO}}{G}\right)^{\alpha} (1 - X_{NO})^{\beta}} \qquad (3)$$

This equation was used in a nonlinear regression computer program, CAL G-2 NLIN, available from the University of California Computer Center Library, to find the combination of parameters (A, E, α, β) which minimized the summation of the squares of the difference between the calculated and experimental nitric oxide conversions (X_{NO}). Because P_{NOi}, P_{HCi}, and W/F_{NO} were not varied for most of the results, only order-of-magnitude changes in A, α, and β, affected the values of the calculated nitric oxide conversions. However, the calculated conversions were quite sensitive to activation-energy variations, and it was therefore concluded that reasonably accurate activation energies were calculated from analysis of the experimental data (*1*). It was observed that with α and β both equal to 0.5, linear Arrhenius plots were obtained for all the NO-hydrocarbon reactions investigated. Correspondingly, values of 0.5 were selected for the reaction orders for all hydrocarbons. The rate expression in all cases was therefore

$$r_{NO} = Ae^{-E/(RT)} P_{HC}^{0.5} P_{NO}^{0.5} \qquad (4)$$

The activation energies (E) and the pre-exponential constants (A) are listed in Table 5 for each NO-hydrocarbon reaction studied.

For comparison, data taken from kinetic studies (*8, 9, 12*) were also fitted to the rate expression found for the NO-hydrocarbon reactions investigated in this study and are presented in Table 5. Using these rate expressions, conversions were calculated for standard reaction conditions (P_{NOi} = 0.01 atm., P_{HCi} = 10% in excess of the stoichiometric requirements, and W/F_{NO} = 6,000 (g.-catalyst)(min.)/g.-mole NO) over a reaction temperature range of 50° to 800°C. These results are presented in Figure 8. Also included in Figure 8 are results for the NO-carbon monoxide reaction based on the data of Ayen and Ng (*7*).

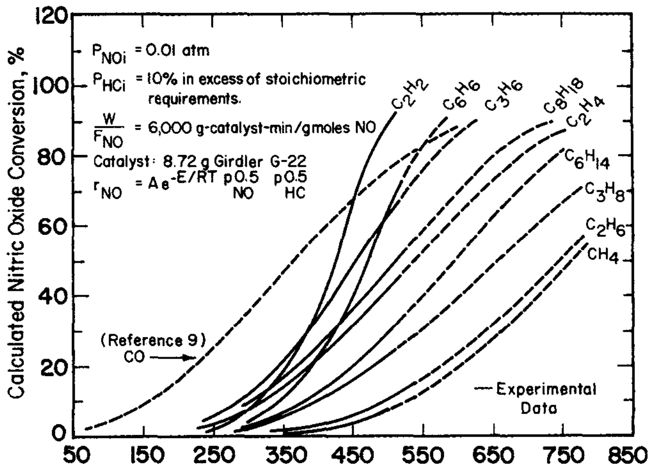

Fig. 8. Comparison of ease of catalytic reduction of nitric oxide by various hydrocarbons and carbon monoxide.

Accomazzo and Nobe (3), in a study concerning the oxidation of light hydrocarbons, observed that methane was the most difficult hydrocarbon to oxidize with air, requiring temperatures greater than 400°C. for appreciable conversion. Figure 8 indicates that the oxidation of methane with nitric oxide is not appreciable until the reaction temperature is raised to 600°C. A similar result was observed with C_2H_2.

CONCLUSIONS

1. Barium-promoted copper chromite appeared to be an efficient and stable catalyst for the reduction of nitric oxide with hydrocarbons.
2. In the catalytic reduction of nitric oxide with methane, ethane, ethylene, acetylene, propane, propylene, *n*-hexane, benzene, and *n*-octane, the products of the overall reaction were essentially carbon dioxide, nitrogen, and water for the conditions encountered in this study.
3. An increase in carbon number for the hydrocarbons investigated decreased the required temperature for a given nitric oxide conversion.
4. For a given carbon number, the required temperature for a given nitric oxide conversion decreased with the degree of saturation of the hydrocarbons studied.
5. For the NO-hydrocarbon reactions investigated, adequate data correlations were obtained with an empirical order-type rate expression:

$$r_{NO} = Ae^{-E/(RT)} P_{NO}^{0.5} P_{HC}^{0.5}$$

6. Different catalyst deactivation rates were observed for each NO-hydrocarbon reaction. The highest decline in catalyst activity was found for the NO-acetylene reaction. Activity was largely restored by short-term treatment with hydrogen.

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NOTATION

A = pre-exponential constant, g.-mole NO converted/(g.-catalyst) (min.) (atm.)$^{\alpha+\beta}$
B = number of moles of nitric oxide that are required to react with one mole of the reducing agent, assuming the reaction products are CO_2, N_2, and H_2O
E = apparent activation energy, cal./g.-mole
F_{NO} = moles of nitric oxide fed to reactor, g.-moles/min.
G = one plus fractional excess of the stoichiometric requirements of the reducing agent
K_{HC} = hydrocarbon or reducing agent adsorption equilibrium constant, atm.$^{-1}$
K_{NO} = nitric oxide adsorption equilibrium constant, atm.$^{-1}$
k = rate constant, g.-moles NO converted/(g.-catalyst) (min.) (atm.)$^{\alpha+\beta}$
P_{HC} = hydrocarbon or reducing agent partial pressure, atm.
P_{NO} = nitric oxide partial pressure, atm.
R = gas constant, cal./(g.-mole) (°K.)
$r_{C_2H_6}$ = reaction rate, g.-mole C_2H_6 reacted/(g.-catalyst) (min.)
r_{HC} = reaction rate, g.-moles hydrocarbon reacted/(g.-catalyst) (min.)
r_{NO} = reaction rate, g.-moles NO converted/(g.-catalyst) (min.)
T = reaction temperature, °K. or °C.
X_{NO} = fractional conversion of nitric oxide
W = weight of catalyst, g.

Greek Letters

α = order of reaction with respect to hydrocarbon or reducing agent, dimensionless
β = order of reaction with respect to nitric oxide, dimensionless

Subscripts

HC = hydrocarbon or reducing agent
i = value in feed stream

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