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A Low Temperature Catalytic Approach to NO_x Control

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Application of catalysts in the control of CO and hydrocarbon emission from vehicles is well established; however, rapid catalytic decomposition of NO_x under these oxidizing conditions remains to be achieved. The role of CO as a reducing agent is only significant in cases where excess CO is present, due to its more rapid oxidation by excess O_2 than by NO_x.

The present study confirms that no appreciable catalytic decomposition of NO or NO_2 to N_2 and O_2 occurs in moist air at temperatures from 200 to 600°C. However, the limiting factor here is suggested to be the presence of water vapor, not excess O_2. In the absence of water vapor, catalytic decomposition of NO_x to N_2 and O_2 occurs in air at normal reaction temperatures due apparently to the presence of an N_2O_4 surface complex. When water vapor is present, it is suggested that N_2O_4 does not form N_2 and O_2 due to splitting of the molecule with water at the N–N bond to form acid intermediates. The existence of HNO_2 and HNO_3 intermediates is demonstrated, which, at elevated temperatures, revert to NO and NO_2. At temperatures less than 100°C, however, HNO_2 becomes a stable gas-phase species, and it appears that rapid catalytic decomposition of this species can be achieved. Although the observed rates are not yet fast enough for satisfactory operation in vehicular exhaust control, the approach shows promise for application as a tail pipe catalyst in NO_x control.

INTRODUCTION

Control of the nitrogen oxides emitted from vehicular exhausts has become increasingly important as more stringent criteria are established by government, based on health factors and the role of NO_x in the formation of photochemical smog, lacrimators, irritants, etc. Among the approaches being investigated for such control is the catalytic decomposition of NO_x to N_2 and O_2. Many automobile and oil companies are directing their efforts to the catalytic reduction of NO_x with CO concentrations in excess of the O_2 present. This is necessary because of the more rapid oxidation of CO by O_2 than by NO_x. However, problems arise from deterioration of the catalyst if not protected from excessive temperatures during high speed cruising, and from the ineffectiveness of the catalyst during cold engine starts. The use of this system to control NO_x emission from diesel engines would be impossible due to the lower levels of CO and high concentration of O_2 found in this exhaust. All these factors point to a need for a better solution to the problem.

At present, legislation for the control of NO_x in the U. S. A. has set a proposed standard for 1976 vehicles of less than 1 g NO_x per vehicle mile. The average NO_x emission from an uncontrolled internal combustion engine (I.C.E.) is about 4 g/vehicle mile. This corresponds to a concentration of 1000–2000 ppm NO_x, most of which is in the form of nitric oxide. It is desirable, particularly for a diesel engine, that the catalytic decomposition of NO_x should be effected in the presence of O_2 and H_2O. It has been calculated that a catalyst effective in reducing the NO_x emission by 3 g/mile, should have a rate of reaction of about 1.5×10^{-7} moles m^{-2}

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min^{-1}. This is based on 4 kg catalyst with a surface area of 150 m^2 g^{-1} and concentrations similar to that found in vehicular exhaust. The low temperature approach to control proposed here should make it possible for surface areas of this magnitude to be maintained in the tail pipe section of the exhaust, and when it is considered that a full tank of gasoline weighs *ca.* 50 kg, the use of catalyst beds larger than that suggested here is not unfeasible although undersirable. Most of the literature on this subject is related to the reduction of NO_x with CO, but Shelef and co-workers at Ford, Michigan, attempted the direct decomposition of NO on a variety of catalysts in an atmosphere of helium (*1*). The observed rates were very low, measured at high NO concentrations, low flow rates, and temperatures of 300–600°C. First-order kinetics were observed, and if the rates are extrapolated to concentrations of 2000 ppm then values of the order of 10^{-12} moles m^{-2} min^{-1} are found, i.e., some five orders of magnitude too slow to be effective. Extensive catalyst screening by other workers (*2*) gave rise to similar results, and it appears that a reasonably fast reaction rate is found only at high temperatures (>800°C) (*3*, *4*), or at high pressures (*5*). The catalytic decomposition of NO_2 has been reported by Wikstrom and Nobe (*6*), who observed fast rates of reaction at low concentrations and temperatures of 300–500°C on CuO and CeO_2 supported catalysts.

EXPERIMENTAL

The apparatus used in our study, Fig. 1, was designed so that mixtures of NO, NO_2, or N_2O_3, in various carrier gases, prepared under dry or wet conditions, could be passed through a fixed bed reactor. For operation under dry conditions, all gases were passed through molecular sieve drying towers. For wet conditions, the carrier gases were saturated with water vapor by passing through two series-connected water bubblers before mixing took place with the NO_x. A bypass section allowed the inlet concentration of the NO_x to be measured at any time and compared with the effluent value when the flow was diverted through the reactor. Analysis of the effluent gases was made with a Model 5750 Hewlett Packard gas chromatograph, an A.E.I. MS10 mass spectrometer, and a Faristor NO_x analyzer manufactured by Envirometrics Corporation, and more familiarly known as the "nox-box." The latter instrument is an electrochemical transducer in which the direct electrooxidation or electroreduction of adsorbed gas molecules at a sensing electrode results in a current directly proportional to the partial pressure of the gas being monitored. None of these methods distinguished between NO and NO_2, and only total NO_x was measured in a mixture of these gases (*7*). The reactor contained *ca.* 15 g catalyst, many of which were commercial Girdler catalysts supported on alumina. Two of the catalysts were prepared in this laboratory: a CeO_2/Al_2O_3 catalyst prepared according to the method suggested by Wikstrom and Nobe (*6*), and a $Ag/Ag_2O/Al_2O_3$ catalyst prepared by soaking 50 g Kaiser KA-201 activated alumina, 8–16 mesh, in a 2.3 *M* solution of $AgNO_3$ for several hours, followed by decantation, drying, and firing at 450°C. The latter catalyst contained 14 g Ag/Ag_2O on 50 g Al_2O_3. Surface areas were measured with an Orr surface area analyzer Model 2100 manufactured by Micromeritics Instrument Corporation.

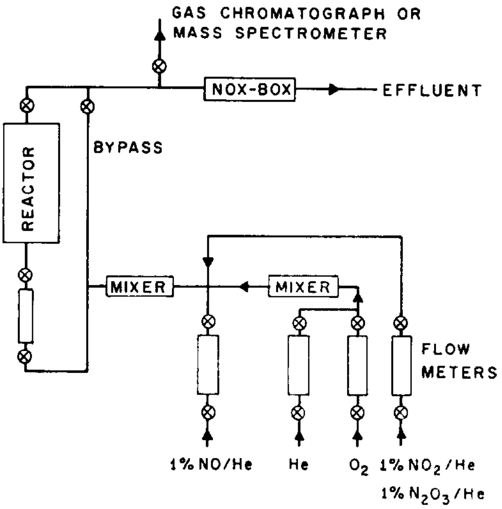


FIG. 1. Schematic of apparatus.

RESULTS AND DISCUSSION

Reactions in Absence of Water Vapor

First attempts at catalyst screening showed that no decomposition could be observed on any catalyst studied at temperatures ranging from 200 to 600°C with an inlet concentration of 2400 ppm NO/moist air, and contact times as long as 3 sec. A similar result was found under the same conditions when NO_2 was used as the starting material, even on the CeO_2 catalyst used by Wikstrom and Nobe. However, when elaborate precautions were taken to dry all of the gases, then a different result was obtained. An attempt was made to remove adsorbed water from a Girdler G.13 copper chromite catalyst by heating it at a temperature of 340°C in a flow of dry helium. When 1000 ppm of NO_2 in a dry He/O_2 mixture (4:1) was passed over this catalyst extensive decomposition was observed at temperatures ranging from 200 to 300°C. He/O_2 was used as a carrier gas so that N_2 could be observed as a product. The mass balance between reactants and products was correct within about 20%. When the concentration of the NO_2 was varied at a fixed reaction temperature of 320°C, then first-order kinetics were observed. The Arrhenius plot is shown in Fig. 2. The activation energy of 28.8 kcal $mole^{-1}$ can only be regarded as an approximate figure since it was not known how much water still remained in the system to poison the reaction, and also at the higher temperatures the extent of either thermal or catalytic dissociation of NO_2 into NO and O_2 was not known.

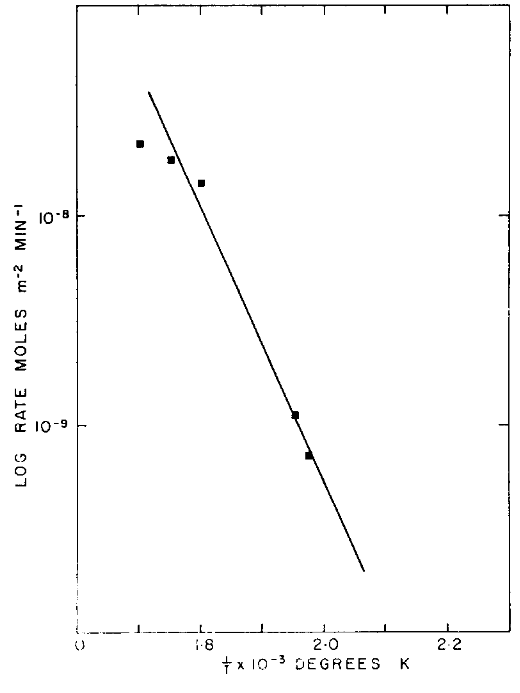
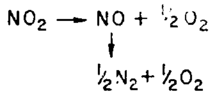


FIG. 2. Arrhenius plot for the dry decomposition of 1000 ppm $NO_2/He/O_2$ over a copper chromite catalyst.

The equilibrium conversion of NO_2 into NO and O_2 becomes appreciable at 300°C and is complete at 600°C (*8*). Wikstrom and Nobe's results (*6*) for NO_2 decomposition were quoted at temperatures of 300–500°C. However, there is clearly some danger of error in operating in this temperature range unless it is known that the direct decomposition of NO_2 to N_2 and O_2 occurs at a rate faster than the conversion to NO and O_2. It seems unlikely as suggested by these authors, that the decomposition takes place:



$$\begin{array}{l} NO_2 \rightarrow NO + \tfrac{1}{2}O_2 \\ \qquad\qquad \downarrow \\ \qquad\quad \tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 \end{array}$$

because of the reported difficulty (*1*, *2*) in catalytically decomposing NO in this temperature range. The production of NO from NO_2, however, is likely to be rapid in this temperature range and, it will be shown later, could be enhanced by the presence of water vapor.

Table 1 summarizes the results when other nitrogen oxides were used as starting materials. A 4:1 ratio of He/O_2 was used in each case. For comparison, the rates are quoted at a temperature of 320°C but similar activation energies were observed in each case. The rate for NO/dry He/O_2 was only one quarter of that for NO_2 demonstrating that only partial oxidation to NO_2 had occurred. In the absence of O_2 no decomposition occurred. The $N_2O_3/He/O_2$ gave rise to a rate similar to that of $NO/He/O_2$, and, again in the absence of

TABLE 1

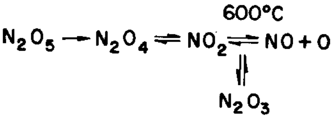
Rate Comparison of the Dry Decomposition of 1000 ppm Nitrogen Oxides in He/O_2 Mixtures Over a Copper Chromite Catalyst at 320°C

He/O_2 ratio 4:1

Species of NO_x	Rates (moles m^{-2} min^{-1})
$NO_2/He/O_2$	2.1×10^{-8}
$NO/He/O_2$	6.5×10^{-9}
NO/He	Not detectable
$N_2O_3/He/O_2$	5.6×10^{-9}
N_2O_3/He	Not detectab'e

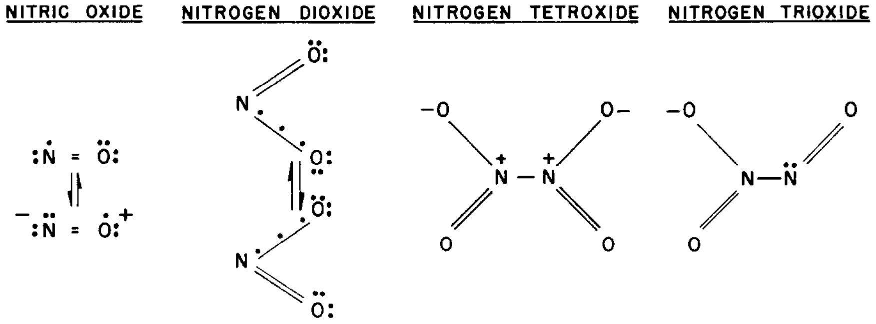
O_2 no decomposition was observed. This demonstrates that under dry conditions NO_2 is a catalytically active species at normal reaction temperatures, but NO and N_2O_3 are not.

The situation is made clearer by examing the structures and interactions which can occur between the various nitrogen oxides. Gas-phase equilibrium occurs between the species:



$$N_2O_5 \longrightarrow N_2O_4 \rightleftharpoons NO_2 \overset{600°C}{\rightleftharpoons} NO + O \qquad NO_2 \rightleftharpoons N_2O_3$$

Thus, at temperatures above 600°C, NO is the only stable species, but at lower temperatures the formation of N_2O_4 is favored. The structure (*8*, *9*) of these molecules is shown below.



The extreme gas-phase stability of nitric oxide, may in part be due to the resonance stability of the two structures shown. The dimer is known only at very low temperatures (*10*). It is apparent that any adsorbed species also exhibits extreme stability, and can be catalytically decomposed only at highly elevated temperatures. Nitrogen tetroxide on the other hand is known to exist in the gas phase at temperatures up to 150°C, and it is quite conceivable that at higher temperatures, nitrogen dioxide can form a surface dimer of N_2O_4. It is clear that the stoichiometry, and the partial formation of the N–N bond in this species should allow the observed dissociation to N_2 and O_2 to take place according to

$$N_2O_4 \longrightarrow N_2 + 2O_2 \qquad (1)$$

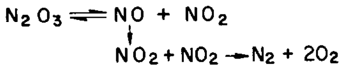
Nitrogen trioxide exists in equilibrium with NO and NO_2:

$$N_2O_3 \rightleftharpoons NO + NO_2 \qquad (2)$$

and requires further interaction with another molecule of N_2O_3 in order that the reaction

(3)

may proceed. This is configurationally improbable and explains the inactivity of this species in the absence of oxygen for the dry decomposition into N_2 and O_2. The equilibrium concentration of NO_2 under these conditions is probably too low to allow observation of any decomposition, and it is also likely that gas phase NO_2 will interact with adsorbed NO to form inactive adsorbed N_2O_3, further reducing the number of adsorbed N_2O_4 species which produce N_2 and O_2. The N_2O_3/air mixtures decompose much like NO/air mixtures, and this can be attributed to oxidation of the NO arising from the equilibrium (2). Thus,

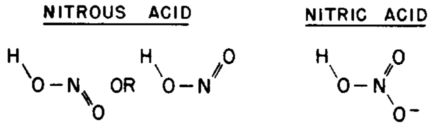


$$N_2O_3 \rightleftharpoons NO + NO_2 \qquad NO_2 + NO_2 \rightarrow N_2 + 2O_2$$

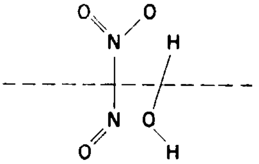
As the reaction proceeds, the equilibrium (2) is displaced to form more NO which is again oxidized to NO_2. The decomposition of N_2O_3, therefore, proceeds at a reasonable rate only in the presence of dry O_2.

Reactions in the Presence of Water Vapor

When water vapor is present, a different set of reactions can be generated involving acid formation. The structure of nitrous and nitric acids are shown below.



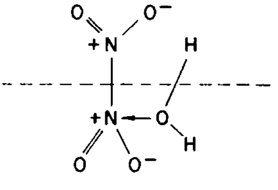
It is proposed that nitrogen trioxide can be split at the N–N bond by a water molecule to form nitrous acid, thus



(4)

$$N_2O_3 + H_2O \rightleftharpoons 2HNO_2$$

This equilibrium is well known in the gas phase and has been extensively studied by Wayne and Jost (*11*). At temperatures above 100°C, this equilibrium lies well to the left. It is similarly proposed that the formation of N_2 from the nitrogen tetroxide surface complex is inhibited by water which again splits the N–N bond to form nitrous and nitric acids:



(5)

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3$$

The HNO_3 vapor is in equilibrium with its anhydride N_2O_5 which readily breaks down to N_2O_4 and NO_2. At elevated temperatures, the HNO_2 will also dissociate according to the equilibrium (4) to form NO and NO_2. Thus, when water is present, no catalytic decomposition of NO_2 occurs to N_2 and O_2 in a temperature range of 200–600°C, but the NO_2 can be partially converted to NO according to reaction (5) and equilibrium (4). For a given temperature, therefore, the rate at which the NO_2/NO equilibrium ratio is reached can be enhanced by the presence of water vapor.

Low Temperature Decomposition in Presence of Water Vapor

At temperatures less than 100°C, an unusual phenomenon was observed on a silver catalyst supported on Kaiser KA-201 activated alumina. When a moist $NO/He/O_2$ mixture (He/O_2 ratio = 4:1) was passed over this catalyst, it was found that after an initial period of adsorption a steady-state conversion was reached which varied with temperature in the manner shown in Fig. 3. Plots A, B, and C, show the effect at temperatures of 25, 70, and 100°C, respectively. For comparison, plot D shows the result at 25°C in the absence of water vapor. In the presence of water vapor, the rate of removal of NO_x from the gas stream decreased with increase in temperature. Nitrogen was observed as a product, but there was insufficient nitrogen to account for the disappearance of all of the NO_x. 500 ppm N_2 was observed at the outlet, whereas some 800 ppm should have been observed to achieve the correct mass balance. It was clear that more NO_x was being removed than could be accounted for by simple adsorption, and it was suspected that acid formation, according to the mechanisms described earlier, was resulting in incorporation of the NO_x in the silver in the form of silver nitrate. Accordingly, after 6 hr of operation at 25°C, the catalyst was removed from the reactor and heated in 20 ml water in an attempt to put into solution any silver nitrate or nitrite formed on the catalyst. Silver nitrate is very soluble in water, and silver nitrite is soluble in

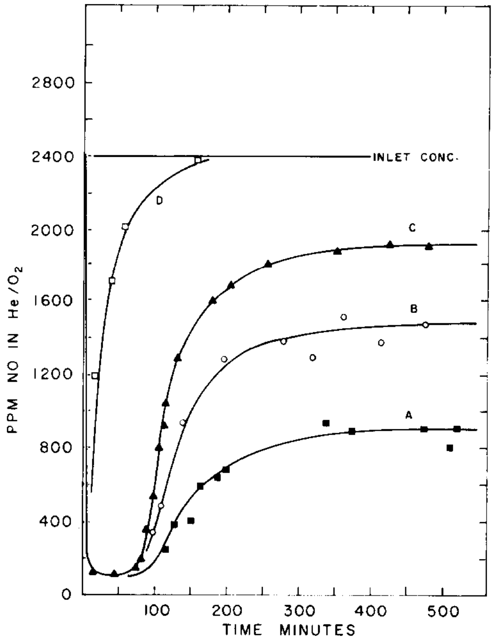


FIG. 3. Effluent NO concentration from the reactor at: A, 25°C, wet; B, 70°C, wet; C, 100°C, wet; D, 25°C, dry; for an inlet concentration of 2400 ppm NO/He/O_2. Flow rate 800 ml min^{-1} over 15 g $Ag/Ag_2O/Al_2O_3$ catalyst, surface area 150 m^2 g^{-1}.

hot water, but relatively insoluble in cold water. After heating for 10 min the solution was filtered hot, and on cooling silver nitrite crystals were observed to precipitate from the solution. The crystals were identified by X-ray crystallography and estimated gravimetrically. Nitrate ion in the solution was estimated with a specific ion electrode apparatus. The catalyst was heated in a further aliquot of water, and the procedure repeated until the detection of NO_3^- and NO_2^- ions was negligible. The complete analysis is shown in Table 2. In 6 hr operation, 0.015 mole NO was removed from the gas stream of which 0.011 mole was decomposed and the remainder taken up by the metal as NO_3^- or NO_2^- ion. From the NO adsorption studies of Shelef (*12*), it has been calculated that for our catalyst the maximum adsorption capacity is 0.005 mole NO. Under dry conditions, this low-temperature decomposition was not observed (plot D, Fig. 3), and after a period of about 2 hr, no further NO was removed from the gas stream by the catalyst. Analysis of the catalyst revealed that only NO_2^- was present on the surface equivalent to 0.005 mole NO, which corresponds with the figure for an adsorbed monolayer and also with the amount of NO removed from the gas stream.

TABLE 2

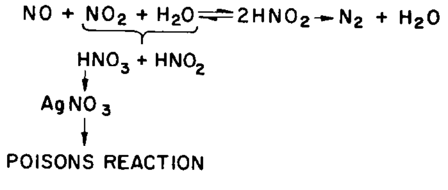
EXTENT OF DECOMPOSITION/INCORPORATION OF 2400 PPM NO IN He/O_2/H_2O ON A SILVER CATALYST AT 25°C AFTER 6 HR (PLOT A, FIG. 3) He/O_2 RATIO 4:1

Total NO removed from gas stream = 0.015 mole
NO removed as NO_3^- ion = 0.0013 mole
NO removed as NO_2^- ion = 0.0026 mole
∴ NO removed by decomposition = 0.011 mole

The observation of NO_3^- ion under moist conditions lends support to the theory that water interacts with adsorbed N_2O_4 to form HNO_3 and inhibit the decomposition to N_2 and O_2. However, at temperatures less than 100°C the equilibrium

$$NO + NO_2 + H_2O \rightleftharpoons 2HNO_2$$

shifts to the right. The kinetics and equilibrium constant of this gas-phase reaction at 25°C have been studied by Wayne and Jost (*12*), who observed half times as short as 0.014 sec. It is clear that in our system HNO_2 could be a stable gas-phase species, and it seems likely that this is the active species involved in the low-temperature decomposition. In nitric acid, the nitrogen atom is fully saturated in its bonding, but with nitrous acid a degree of unsaturation remains on the nitrogen atom permitting interaction with another nitrous acid molecule or with an adsorbed NO_2^- ion and resulting in decomposition of the complex formed. A competitive reaction of NO_2 with water also occurs to form HNO_3, so that the complete reaction scheme is represented schematically:



The competitive reaction to form HNO_3 results in undesirable NO_x emission and, in the case of the silver catalyst poisons it by building up silver nitrate.

An alternative explanation based on surface disproportionation reactions (*13*, *14*) such as

$$4NO \longrightarrow N_2O + N_2O_3 \xrightarrow{H_2O} HNO_2$$
$$\text{OR} \quad 4NO \longrightarrow N_2 + 2NO_2$$

seems unlikely in this case as N_2O was not observed as a product in the mass spectrum. In addition, such disproportionation reactions would continue to take place in the absence of O_2, whereas with the present catalyst, when O_2 was excluded from the reaction mixture containing only NO and He, the low-temperature decomposition was not observed. An oxidation step is, therefore, necessary when NO is used as starting material, but whether this takes place in the gas phase or is a surface reaction, cannot be concluded from our results. The results of a long term experiment on this catalyst at 25°C run for 100 hr is shown in Fig. 4.

The rate of removal of NO from the gas stream slowly decreases with time as more $AgNO_3$ is formed, and, after 50 or 60 hr, reaches a constant value. After 100 hr the catalyst was analyzed for NO_3^- and NO_2^- ion. No NO_2^- was detected. The amount of NO_3^- detected was only slightly greater than the theoretical amount required to react with all of the Ag to form $AgNO_3$. At the rate of formation of $AgNO_3$ determined on the 6-hr catalyst, it was expected that all of the silver would be converted to the nitrate after about 60 hr, which corresponds fairly well with the time over which the catalyst lost activity (Fig. 4) before reaching a constant value. The constant reaction rate finally observed was measured more accurately at lower flow rates, and clearly must be that taking place on the bare alumina surface. Over the last 40 hr of the experiment, therefore, 0.017 mole NO was removed by decomposition on the alumina. Over the total 100 hr experiment, 0.043 mole NO would therefore have decomposed on the alumina. Since 0.036 mole NO had reacted with the silver to form $AgNO_3$, and since the total NO removed from the gas stream during the 100 hr was 0.133 mole, then clearly 0.054 mole NO must have decomposed on the silver during the first 60 hr operation. The complete analysis is shown in Table 3. It is also possible that not all of the silver was converted to silver nitrate and that the NO_3^- ion detected on the catalyst arose from two sources; i.e., from $AgNO_3$ and from adsorbed HNO_3. In either case, it is clear from the mass balance and from the detection of N_2 as a product of the

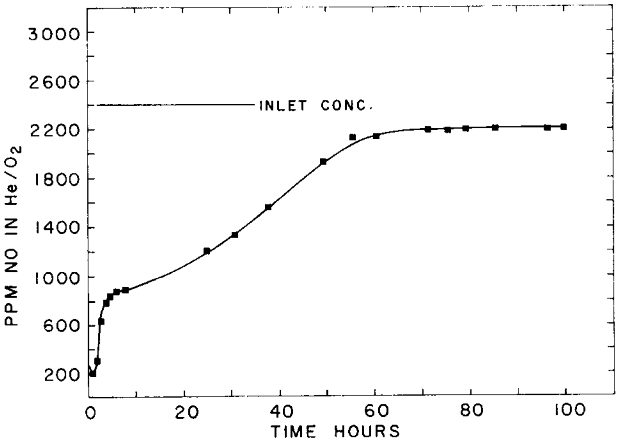


FIG. 4. Effluent NO concentration from reactor at 25°C containing 15 g $Ag/Ag_2O/Al_2O_3$ catalyst measured over a period of 100 hr with an inlet concentration of 2400 ppm $NO/He/O_2/H_2O$, flow rate 800 ml min^{-1}, surface area 150 m^2 g^{-1}.

TABLE 3
Extent of Decomposition/Incorporation of 2400 ppm NO in $He/O_2/H_2O$ on a Silver Catalyst at 25°C after 100 hr Operation (Fig. 4)
He/O_2 ratio 4:1

Total NO removed from gas stream = 0.133 mole
NO removed as NO_2^- ion = Not detected
NO removed as NO_3^- ion = 0.045 mole
Theoretical NO removed as NO_3^- ion for complete reaction with Ag = 0.036 mole
NO removed by decomposition on Al_2O_3 = 0.043 mole
∴ NO removed by decomposition on Ag = 0.045 mole

reaction, that rapid decomposition of the HNO_2 occurred on the silver before it was poisoned with the HNO_3.

The fact that the final rate observed on the silver catalyst was likely to be due to reaction on the alumina was confirmed by filling the reactor with untreated alumina and carrying out the experiment with the same $NO/He/O_2$ mixture. The surface area of the untreated alumina was large (320 m^2 g^{-1}) and so the degree of conversion appeared high and remained constant in contrast to the results on the silver catalyst. The rate of loss of NO measured on the alumina surface was the same as the final rate measured on the silver catalyst confirming that the latter reaction was taking place on the alumina surface of the silver catalyst. These rates, and the initial rate on the silver catalyst are shown in Table 4. It is of interest to note that if cylinder N_2O_3 is used as a starting material instead of NO, then the rate (Table 4) is considerably faster. This supports the idea that HNO^2 is the active species, as the stoichiometry for the formation of HNO_2 is favored when N_2O_3 is used as a starting material compared with $NO/He/O_2$ mixtures. In this case, also, the competitive reaction to form HNO_3 will be reduced. Also shown in Table 4 is the rate observed on a platinum catalyst, which did not exhibit any poisoning characteristic. This may result from a more favorable pore distribution which allows decomposition of the HNO_2 within selective pores, but excludes the HNO_3 from reaching the active area with subsequent poisoning. However, compared with the target figure of 1.5×10^{-7} moles m^{-2} min^{-1}, although these rates are now approaching the right order of magnitude for practical application they are still too slow to be acceptable.

Conclusion

In the absence of water vapor, N_2O_4 appears to be an active species in the catalytic decomposition of NO/air mixtures at normal reaction temperatures. The other oxides of nitrogen are inactive. When water vapor is present N_2O_4 becomes inactive due to splitting of the molecule to form acid intermediates, and at temperatures above 100°C can only be converted into the extremely stable nitric oxide. At temperatures less than 100°C a new species, HNO_2, becomes stable in the gas phase, and it appears that this can be catalytically converted to N_2 and H_2O. This low temperature approach shows promise for application to vehicular exhaust control. Present engine modifications minimize CO and hydrocarbon emission which can be further reduced with a suitable oxidation catalyst in the muffler section of the exhaust. In this approach, NO_x would then be removed with a tail pipe catalyst. The system has

TABLE 4
Rate Comparison of the Wet Decomposition of 2400 ppm Nitrogen Oxides in He/O_2 Mixtures Over Silver, Platinum and Alumina Catalysts at 25°C
He/O_2 ratio 4:1

Desired rate for practical application based on 4 kg catalyst, 150 m^2 g^{-1} = 1.5×10^{-7} moles m^{-2} min^{-1}
Initial rate on Ag catalyst: 2400 ppm $NO/He/O_2$ = 1.2×10^{-8} moles m^{-2} min^{-1}
Final rate on Ag catalyst: 2400 ppm $NO/He/O_2$ = 3.25×10^{-9} moles m^{-2} min^{-1}
Rate on Alumina: 2400 ppm $NO/He/O_2$ = 2.75×10^{-9} moles m^{-2} min^{-1}
Rate on Alumina: 2400 ppm $N_2O_3/He/O_2$ = 4.5×10^{-9} moles m^{-2} min^{-1}
Rate on Pt catalyst: 2400 ppm $N_2O_3/He/O_2$ = 9.0×10^{-9} moles m^{-2} min^{-1}

a number of advantages such as ease of catalyst replacement or servicing, and effective performance under all engine operating conditions. It will also be effective for diesel engines in contrast with the CO reduction control method. Although the observed rates are not yet fast enough for satisfactory operation, they are approaching the correct order of magnitude for practical application, and it is hoped that catalyst screening will reveal a suitable catalyst more selective in decomposing the HNO_2 which is unaffected by, and excludes HNO_3 poisoning.

ACKNOWLEDGMENTS

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