Nitric Oxide Reduction with Methane over Pd/TiO$_2$ Catalysts

I. Effect of Oxygen Concentration

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Steady-state reaction studies were performed over a Pd/titania catalyst for NO reduction using CH$_4$ as a reducing agent. The catalyst was prepared using a wet impregnation technique and Pd-acetate as a precursor for palladium. Characterization of the catalyst samples was performed using the BET surface area technique, X-ray diffraction (XRD), laser Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and thermal analysis techniques. A fixed-bed, flow reactor system was used for activity and selectivity measurements. Identification and quantification of reaction effluents were done on-line using gas chromatography–mass spectrometry, chemiluminescence, and wet chemistry techniques. Temperature-programmed reduction studies indicated that the catalyst was reducible by H$_2$ even at sub-ambient temperatures. The catalyst was seen to reduce NO with conversions above 95% in the oxygen concentration range from 0 to 1.3%. Oscillatory behavior was exhibited by the catalyst under certain reaction conditions. The results obtained from the reaction experiments, together with the findings from the characterization studies, are used to explain the mechanistic aspects of this reaction. © 1997 Academic Press

INTRODUCTION

Recently there has been growing interest in reducing NO$_x$ emissions using hydrocarbons from stationary sources. Several hydrocarbons have been investigated as reducing agents for NO$_x$ reduction to replace the current process which utilizes ammonia (1–6). There are several disadvantages associated with using ammonia as a reducing agent. The main problem is the corrosion of downstream equipment due to formation of ammonium salts as a result of a reaction of SO$_x$ and NH$_3$ present in the gas stream. The other concerns are associated with transportation and storage of ammonia in and around residential areas and slippage of unreacted ammonia. The use of hydrocarbons offers obvious practical advantages over ammonia.

Methane being the most abundant hydrocarbon in the form of natural gas offers a very attractive alternative for NO$_x$ reduction. Recently, several catalysts have been investigated for this reaction. Some of the promising catalysts investigated include Co-ZSM-5 (7), Co-ferrierites (8), Ga-ZSM-5 (9), rare earth oxides (10), and Pd-ZSM-5 (11, 12). The kinetics and mechanism of the NO–CH$_4$ reaction seem to be a strong function of the nature of the catalyst, including its active component and the support. Li and Armor (7) have studied zeolites such as mordenite and ZSM-5 exchanged with different ions such as Co^{2+}, Ni^{2+}, and Mn^{2+}. Co-ZSM-5 was seen to be the most active of all these catalysts for NO$_x$ reduction in the presence of excess oxygen. It was also pointed out that cobalt, when impregnated on a conventional oxide support, renders a very poor catalyst for NO$_x$ reduction. Li and Armor (8) have also studied Co-ferrierite which offers a dramatic increase in the activity over the Co-ZSM-5 catalyst. Water was seen to inhibit the activity for both of these catalysts. Another family of catalysts, i.e., methane coupling catalysts, was investigated by Vannice & co-workers for NO reduction with methane (10). Li/MgO, La$_2$O$_3$, CeO$_2$, Nd$_2$O$_3$, Sm$_2$O$_3$, Tm$_2$O$_3$, Lu$_2$O$_3$, and Sr–Sm$_2$O$_3$ were some of the catalysts studied for NO reduction with methane. Li-promoted MgO catalysts were seen to be active in reducing NO in the absence of oxygen, but the activity decreased with the introduction of oxygen in the feed stream. Methane conversion was seen to increase with the introduction of oxygen. Resasco and co-workers (11) observed that prereduced Pd-ZSM-5 was active for NO decomposition, but deactivated rapidly with the product oxygen poisoning the catalyst. Introduction of methane into the system exhibited high and sustained activity for NO reduction in the absence of gas-phase oxygen.

Activation of methane seems to be a crucial step in NO reduction reactions. A good catalyst should activate methane and should be able to selectively reduce NO, even in the presence of gas-phase oxygen. Other desirable

properties of a good NO_x reduction catalyst are thermal and hydrothermal stability under severe conditions. Palladium catalysts are well known for their ability to activate lower hydrocarbons, especially methane, in several complete and partial oxidation reactions. More recently the interest in Pd-based catalysts has increased because of the stricter hydrocarbon emission standards for automobiles and because of their potential use as methane combustion catalysts. Pd-only catalysts for automobiles offer advantages in cost as compared to Rh/Pt catalysts. Another aspect which has stimulated this interest is the scarce supply of Rh and Pt coupled with relatively large supplies of Pd in the United States. It is evident that a better understanding of the $NO/CH_4/O_2$ interaction over Pd-based catalysts would be of significant value.

In our earlier studies, it was shown that NO can be reduced with conversions exceeding 95%, in the absence and in the presence of oxygen over Pd/titania catalysts (13) using methane as a reducing agent. We have also performed isotopic tracer studies to understand the mechanistic aspects of $NO-CH_4$ interaction over these catalysts (14). In this article we report the results of reaction studies over Pd/titania catalysts, where the effect of temperature and oxygen concentration in $NO-CH_4$ reaction was examined, using oxygen concentrations ranging from 0 to 1.3% and temperatures ranging from 200 to 600°C. Although a complete testing of the catalyst would certainly require examining the NO reduction behavior in the presence of water vapor, CO_2, and even SO_x, we have limited the scope of this phase of the study to the assessment of the effect of oxygen concentration. Studies examining the effect of other stack gas components such as water vapor, CO_2, and SO_2 are currently under way.

EXPERIMENTAL

Catalyst Preparation and Characterization

The catalyst used in this study was 2 wt% Pd/TiO_2 which was prepared using a wet impregnation technique. The TiO_2 (anatase) (Aldrich) support was wet impregnated with a solution of Pd-acetate (Aldrich). Oxalic acid was added to the solution to maintain the pH around 4.0. The solution was then stirred at 90°C for 4.5 h, followed by overnight drying of the slurry in the oven at 100°C. The resulting catalyst was then calcined at 500°C (or at the reaction temperature for those cases where the reaction temperature was higher than 500°C) in oxygen for 5 hr. In the experiments which involved bare titania (e.g., TPR, TPD), TiO_2 was used as received, without any further treatment.

The catalyst used in this study was characterized using several techniques such as BET surface area measurements, scanning electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction, laser Raman spectroscopy, and temperature-programmed reduction (TPR) and desorption (TPD) techniques. Details of these studies have been reported elsewhere (15).

Reaction Studies

NO reduction with methane was studied in the presence as well as in the absence of oxygen. The experimental setup used for these studies is described in detail elsewhere (16). The reaction experiments were performed in a fixed-bed, flow reactor. Feed and product analyses were done using a combination of on-line gas chromatography, mass spectrometry, wet chemistry, and chemiluminescence analysis techniques. Inlet and outlet concentrations of nitric oxide were measured with an on-line chemiluminescence $NO-NO_x$ analyzer (Thermo Environmental Instruments, model 10). The ammonia concentrations in the product streams were determined by a conventional titration method with the aid of a hydrochloric acid solution of known concentration after the product stream was bubbled through a diluted aqueous boric acid solution for the absorption of ammonia. An on-line gas chromatograph (Hewlett Packard 5890 A) with a 10 ft × 1/8 in Porapak Q column and a 8 ft × 1/8 in molecular sieve 5Å column was used to quantify N_2, N_2O, CO, CO_2, and CH_4 concentrations.

The weight of the catalyst was varied between 37.5 and 75 mg. The total flow rate of the feed stream was 62 cm^3(STP)/min. This gave a space velocity between 96,000 to 192,000 hr^{-1}. The methane-to-NO ratio was maintained at 12 for all the runs. The catalyst was reduced *in situ* in a stream of hydrogen (33%, balance helium) at 200°C for 30 min, followed by flushing with helium (40 cm^3(STP)/min) at the same temperature for 1 hr before the reaction experiments.
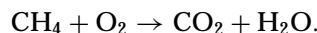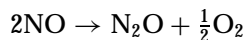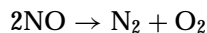
RESULTS

Catalyst Characterization

The catalyst had a surface area of 12.0 m^2/g. X-ray diffraction and X-ray photoelectron spectroscopy studies over the oxidized catalysts have shown that all the palladium on the surface is in the form of palladium oxide (PdO), following the synthesis. All the features in the X-ray diffraction pattern correspond to the anatase phase of TiO_2, with an additional weak signal observed at a *d* spacing of 2.644 Å, which corresponds to the (101) reflection of PdO. The signal was very weak since the metal loading was quite low for the sensitivity limits of this technique. The powder diffraction pattern of the catalyst which was treated with hydrogen at 200°C for 30 min showed, in addition to the peaks that were typical of TiO_2, a small feature at a *d* spacing of 2.246 Å, which corresponds to the (100) reflection of metallic palladium.

The X-ray photoelectron spectra showed that all the palladium present on the surface of a fresh catalyst was in the form of PdO, whereas the surface of a prereduced catalyst comprised mostly of metallic Pd, with only 10.5% being in the form of PdO. Details of catalyst characterization results have been presented elsewhere (15).

Temperature-programmed reduction experiments over oxidized catalyst showed a strong hydrogen consumption peak observed while the temperature of the catalyst was kept around at 5°C, followed by a hydrogen evolution peak (negative peak) seen at around 95°C. Temperature programmed desorption experiments performed without any adsorption steps showed an oxygen evolution feature around 680°C (15).

Reaction Studies

The system studied involves several possible reactions such as

$$4NO + CH_4 \rightarrow 2N_2 + 2H_2O + CO_2$$
$$2NO \rightarrow N_2 + O_2$$
$$2NO \rightarrow N_2O + \tfrac{1}{2}O_2$$
$$CH_4 + O_2 \rightarrow CO_2 + H_2O.$$

Formation of CO and even hydrogen as products is also among the possibilities. This phase of the study was aimed at assessment of the effect of oxygen and of temperature on NO reduction behavior.

For all the runs, the NO and CH$_4$ concentrations were kept constant at 1789 and 21300 ppm, respectively. The closure of carbon balances for all the runs was greater than 95%. The closure of nitrogen balances was greater than 97%.

NO reduction with methane in the absence of oxygen. NO reduction was investigated over 2% Pd/TiO$_2$ catalyst in the absence of oxygen in a temperature range from 200 to 500°C in intervals of 50°C. The space velocity used was 96,000 hr^{-1}. Activity measurements were performed using a feed mixture that consisted of 1770 ppm NO, 2.13% CH$_4$, and the balance helium.

CO, CO$_2$, N$_2$, NH$_3$, and N$_2$O were the only carbon- and nitrogen-containing products observed. The consumption and production rates of various species are presented in Figs. 1a and 1b. There was very little methane conversion observed at 200 and 250°C. At 300°C, the methane conversion was around 1%. It steadily increased with temperature up to 450°C and showed a steeper slope between 450 and 500°C. At this temperature the conversion was around 4.5%. There was no detectable CO$_2$ formation at 200 and 250°C. The CO$_2$ formation increased with temperature up to 400°C and remained essentially constant at higher temperatures. At 500°C, there were significant levels of CO formation, equaling those of CO$_2$ formation. NO conver-
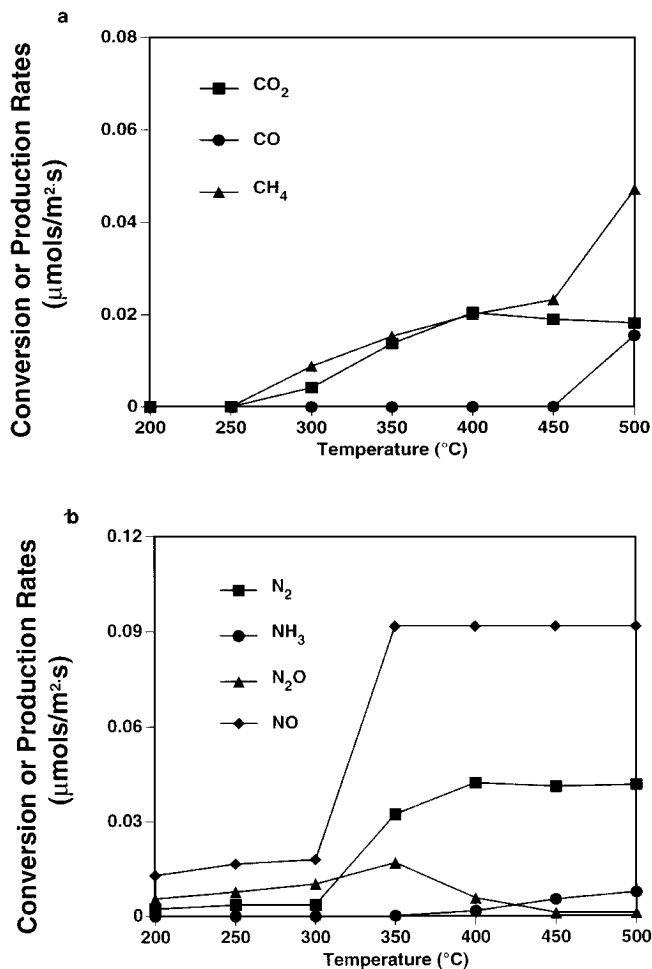
FIG. 1. Conversion and production rates of different species in NO + CH$_4$ reaction in the absence of oxygen (SV = 96,000 hr^{-1}): (a) C-containing species, (b) N-containing species.

sion profiles in the same range are presented in Fig. 1b. Between 200 and 300°C, the NO conversion changed from 10 to 15%. At 350°C, the NO conversion showed a sudden rise, reaching 100%. The NO conversion continued to be complete at higher temperatures. The N$_2$O production rate was slightly higher than the N$_2$ production rate at lower temperatures. Between 300 and 400°C, the N$_2$ production rate increased substantially and leveled off at higher temperatures. N$_2$O formation rate, on the other hand, went through a very broad maximum and became almost negligible above 450°C. There was no NH$_3$ formation observed below 350°C. Its formation rate increased slowly with temperature, accounting for 8.5% of NO in the feed at 500°C (Fig. 1b).

Activity experiments with the same feed mixture were also performed at a higher space velocity (192,000 hr^{-1}). These experiments were performed at 400, 450, and 500°C where NO conversion was complete and there was substantial methane conversion. The selectivities of nitrogen-
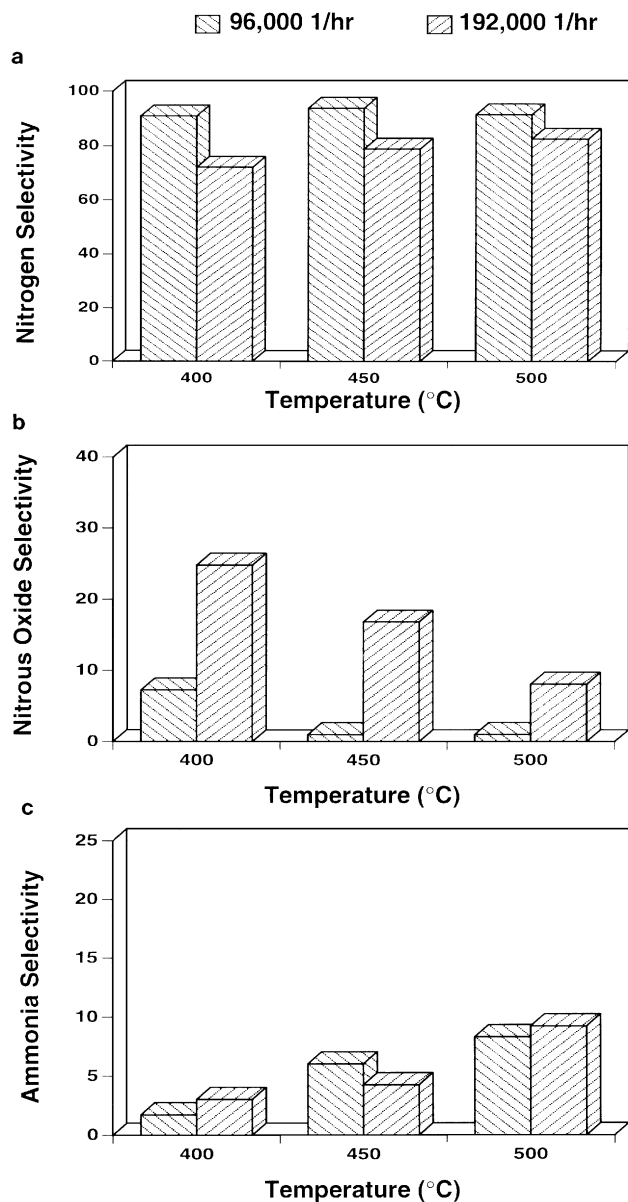
FIG. 2. Selectivities for N-containing products in $NO + CH_4$ reaction in the absence of oxygen: (a) N_2, (b) N_2O, and (c) NH_3.

containing products, i.e., N_2, N_2O, and NH_3, at two different space velocities as a function of temperature are compared in Figs. 2a–2c, respectively. This comparison corresponds to equal conversion of NO, which was ~100% for all cases. In this temperature range, the selectivity to N_2 increases with temperature whereas the selectivity to N_2O decreases. The selectivity to NH_3 also increases with temperature. These trends remain the same at both space velocities. It is also observed that the higher space velocity increases N_2O selectivity, whereas it decreases N_2 selectivity. The percent methane conversion was lower at the higher space velocity, as expected. At 400 and 450°C, CO_2 was the only carbon

containing product, whereas at 500°C, CO formation was observed, with a higher formation rate at the higher space velocity.

NO reduction with methane in the presence of oxygen. NO reduction reactions with methane were also performed in the presence of gas phase oxygen. The oxygen concentration range was varied depending on the temperature of the reaction. Catalytic activity was investigated in the presence of oxygen at three different reaction temperatures, namely 500, 550, and 600°C. The space velocity was kept at 192,000 hr^{-1} for all runs in this set of experiments. At every temperature the oxygen concentration was increased in steps and the activity of the catalyst and its selectivity toward different products were investigated.

One interesting feature observed in the course of the reaction experiments was that, at every temperature, there was a critical oxygen concentration range in which regular, self-sustained oscillations were observed in both reactant and product profiles. Above this oxygen concentration range, the NO conversion level dropped to about 10% and CH_4 conversion increased by almost twofold above its mean oscillatory value. Below the critical oxygen concentration, NO conversion was higher than 98% at every temperature. The conditions under which the oscillatory behavior was observed are listed in Table 1.

At 500°C, the oscillatory behavior was observed when O_2 concentration was raised to 3800 ppm. The reactant and product profiles obtained during this oscillatory behavior under these conditions are presented in Fig. 3. Ions with $m/e = 15$ and $m/e = 30$ were followed for methane and NO profiles, respectively. The profile for the ion with $m/e = 28$ represents a combination of CO and N_2 and the profile for the ion with $m/e = 44$ is a combination of N_2O and CO_2. CH_4 conversion was seen to oscillate between 2 and 16% while the NO conversion was seen to oscillate between 93 and 11%. The average time period of oscillations for all the species was 0.387 min. Temperature oscillations of about 2–3°C were also seen accompanying the oscillations in reactant and product profiles.

TABLE 1

Conditions under Which Oscillatory Behavior was Observed

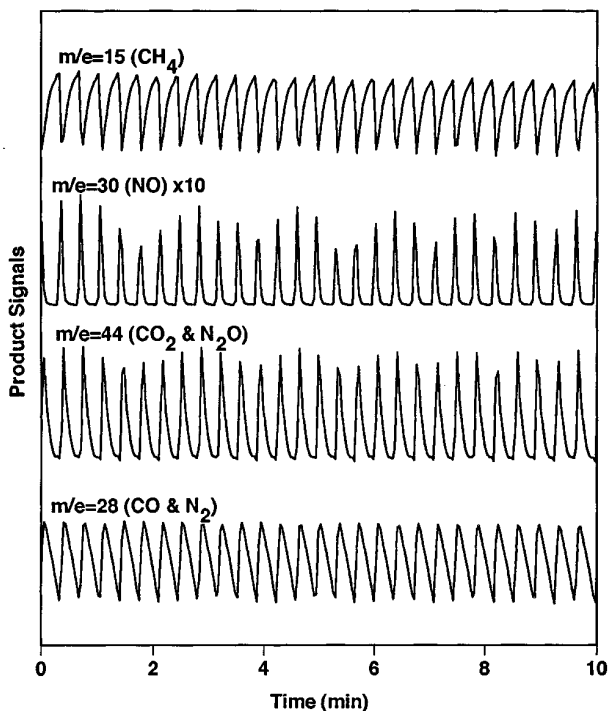| Temp. (°C)	O_2 concentration (%)	Observation
500	0.20	>98% NO conversion
500	0.29	>98% NO conversion
500	0.38	Oscillatory behavior
550	0.38	>98% NO conversion
550	0.70	>98% NO conversion
550	0.87	Oscillatory behavior
600	0.70	>98% NO conversion
600	1.17	>98% NO conversion
600	1.31	Oscillatory behavior

FIG. 3. Reactant and product oscillations in $NO + CH_4 + O_2$ reaction at 500°C ($NO = 1780$ ppm, $CH_4 = 2.12\%$, and $O_2 = 3800$ ppm).

Oscillations observed in the profiles of different species were not completely symmetric. CH_4 and NO oscillations seemed to be out of phase with each other. The oscillations observed in ions $m/e = 28$ and $m/e = 44$ seemed to be roughly in phase with each other and out of phase with CH_4 oscillations.

When the temperature of the catalyst was raised to 550°C, keeping the other parameters constant, the oscillatory behavior disappeared, giving essentially complete NO conversion. At 500°C, the oscillatory behavior was observed between oxygen concentrations of 3800 and 6500 ppm. When the oxygen concentration was raised to 7500 ppm at this temperature, the oscillations disappeared and the NO and CH_4 conversion levels remained at steady values of 10 and 16%, respectively. Definite conclusions cannot be drawn from this set of data since each of the ions ($m/e = 28$ and $m/e = 44$) represents a mixture of two different species. A detailed investigation of this oscillatory behavior conducted using isotopically labeled reactants is presented in a subsequent paper (17).

At 500°C the NO–CH_4 reaction was examined at three different oxygen concentrations, namely, 0, 2095, and 2980 ppm. The rates of conversion and formation of various species are presented in Figs. 4a and 4b. Methane conversion increased from 3.1% in the absence of oxygen to 10.3% in 2980 ppm of oxygen. The CO_2 production rate also increased steadily in the same range. While the net

rate of CO production did not appear to be strongly affected by oxygen concentration, its percentage in the overall product distribution, i.e., selectivity clearly decreased. The NO conversion was over 98% in this oxygen concentration range. The nitrogen and ammonia formation rates remained steady over the oxygen concentration range studied. No appreciable N_2O was detected using a gas chromatograph when there was oxygen present in the feed stream. However, N_2O was observed when the reactor effluent was analyzed using a mass spectrometer.

At 550°C the NO–CH_4 reaction was studied at three different oxygen concentrations, namely, 2095, 2980, and 7000 ppm. The conversion and production rates of various species are presented in Figs. 5a and 5b. Methane conver-
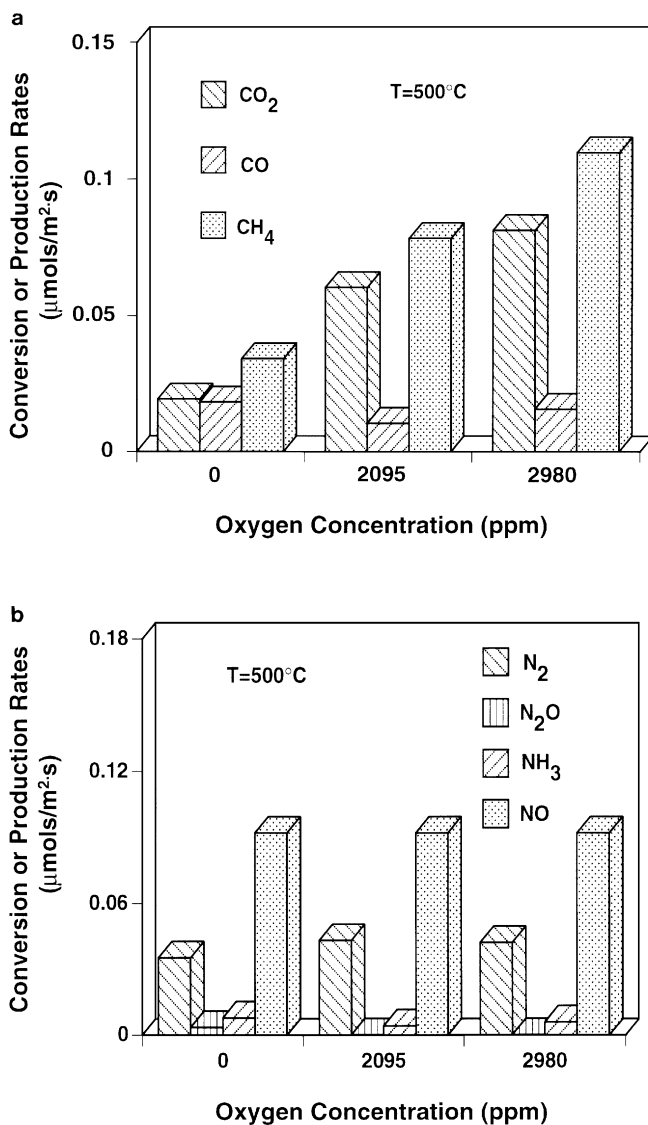

FIG. 4. Conversion and production rates for different species in $NO + CH_4 + O_2$ reaction at 500°C: (a) C-containing species, (b) N-containing species.
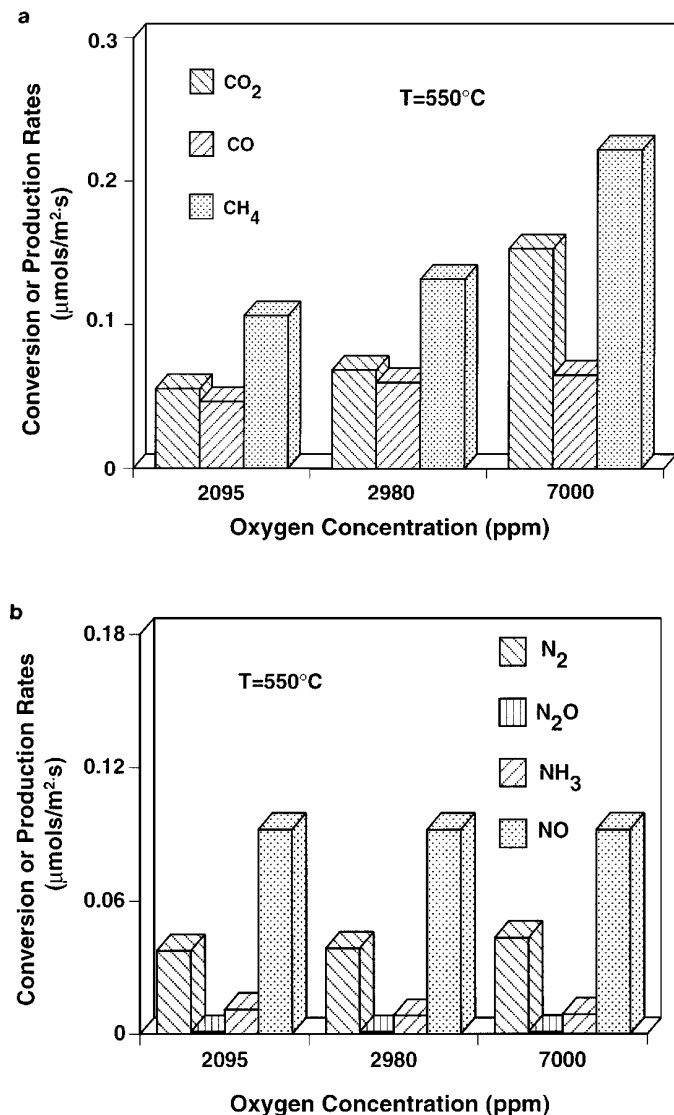
FIG. 5. Conversion and production rates for different species in $NO + CH_4 + O_2$ reaction at 550°C: (a) C-containing species, (b) N-containing species.

by the mass spectrometer. The other trends were similar to those observed at the lower temperatures.

At 500°C and with an oxygen concentration of 2090 ppm, the 63% of CH_4 converted was used for NO reduction and the remaining 37% for complete combustion. The percentage of CH_4 used for compete combustion increased with increasing temperature and oxygen concentration, as expected.

Control experiments. Control experiments performed over freshly oxidized versus prereduced catalysts (Table 2) showed the NO conversion to be very low in the first few minutes over the oxidized catalyst as compared to >98% over the prereduced catalyst in the same time period. Methane conversion on the other hand was significantly higher over the oxidized catalyst initially than it was over the prereduced catalyst. Within the first 20 min, however, the conversion levels over the oxidized catalyst became
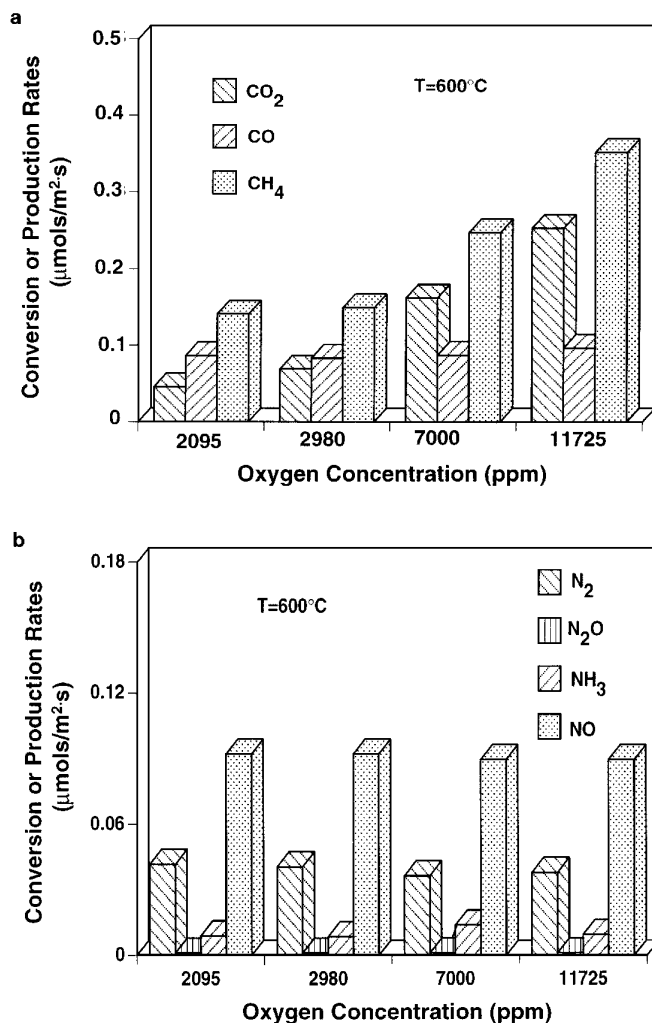
FIG. 6. Conversion and production rates for different species in $NO + CH_4 + O_2$ reaction at 600°C: (a) C-containing species, (b) N-containing species.

sion increased from 9.7% at 2095 ppm of oxygen to 21% at 7000 ppm of oxygen. The conversion of NO at this temperature was essentially complete. The effect of oxygen concentration on product distribution was similar to that observed at 500°C.

At 600°C, the oxygen concentration was varied between 2095 and 11720 ppm. The conversion and production rates of different species are presented in Figs. 6a and 6b. Methane conversion was seen to increase from 13.2% at 2095 ppm oxygen to 36.8% at 11,720 ppm of oxygen. The NO conversion was again essentially complete. While the N_2 was the major nitrogen containing product with a selectivity of 91%, ammonia production remained at nonnegligible levels. N_2O formation was small and was detectable only

TABLE 2

Variation of NO and CH$_4$ Conversion Levels in the First 20 min of the Reaction ($T = 500°$C, NO $= 1780$ ppm, CH$_4 = 2.13\%$, O$_2 = 2100$ ppm)

Time (min)	Oxidized catalyst %conversion		Prereduced catalyst %conversion	
	NO	CH$_4$	NO	CH$_4$
4	<1.0	23.0	99	7.1
6	26	10.8	99	7.1
8	95	7.4	99	7.1
20	99	7.1	99	7.1

equal to the ones observed over the prereduced catalyst. The other interesting feature of these control experiments was that the product distribution of the nitrogen containing species changed in favor of nitrous oxide when a freshly oxidized catalyst was used instead of the prereduced catalyst. Again, the difference between the product distribution of the oxidized and reduced catalysts, which was significant at the beginning of the reaction, became negligible after the first 20 min.

DISCUSSION

The NO−CH$_4$ reaction studies performed over Pd/TiO$_2$ catalysts, when combined with characterization results, strongly suggest that the phase transition between the oxide and the metallic forms of palladium is one of the key factors in determining the catalytic activity of these catalysts in NO reduction reaction.

As seen in the TPR experiments, PdO can be reduced to the metallic phase very easily, even at subambient temperatures. The oxygen signal observed when the oxidized sample is subjected to a temperature-programmed desorption procedure without adsorbing any gases over it is due to thermal decomposition of the palladium oxide to metallic palladium. In the absence of gas phase oxygen, this transition takes place at around 680°C. Similar behavior is observed when Pd is supported over other oxides (26). The phase transition takes place at higher temperatures as the partial pressure of oxygen is increased and in some cases shows a hysteresis when the steps are reversed (27). Some of our later studies conducted using thermal gravimetric analysis (TGA) and controlled atmosphere X-ray diffraction techniques, which showed the relative ease and speed with which the phase transformation can take place between the oxidic and the metallic phases, lend further support to this suggestion (17).

NO−CH$_4$ reaction studies showed that it was possible to achieve complete conversion of NO in the absence as well as in the presence of gas phase oxygen over Pd/TiO$_2$ catalysts. These studies also showed that it was the metallic palladium that was active in reducing NO to N$_2$. The oxide form of the catalyst, however, clearly showed higher activity for methane combustion than the reduced form.

Another important phenomenon that is observed in these studies is the self-sustained oscillations that occur once a critical oxygen concentration level is reached. The oxygen concentration at which the oscillations start to appear goes up with increasing temperature. Although the results presented in this article do not provide any direct evidence as to the cause of these oscillations, our more recent studies (17), combined with some findings in the literature (28–31), lead us to suggest that these oscillations are the result of cyclic phase transformations between the oxidic and the metallic forms of palladium on the catalyst surface.

These observations coupled with the results of some detailed isotopic labeling studies (32) suggest that the reduction of NO to N$_2$ takes place through an interaction between adsorbed NO species and activated CH$_x$ species. The metallic form of palladium is needed to generate and stabilize the CH$_x$ species on the surface, as we have also seen in studies on methane coupling over Pd-promoted catalysts (33). The oxide form of palladium readily combusts methane through the direct involvement of oxygen in the PdO lattice. CH$_x$ species over the oxide either are not generated, or are readily consumed by the combustion reaction and are not available for the NO reduction reaction. The increase in the methane conversion coupled with the dramatic drop in NO reduction when a fully oxidized catalyst is used instead of the reduced one supports this suggestion. Over the metallic palladium sites, however, CH$_x$ species are not only generated, but reside on the surface as evidenced by our transient response experiments (14, 32) and they are essential for reduction of NO to molecular nitrogen. Occurrence and stability of various CH$_x$(s) species over noble metal catalysts have been discussed in detail in the literature (34, 35). At temperatures above 200°C, Solymosi and co-workers have observed methane dissociation into CH$_x$ and H fragments over Pd surfaces and have reported Pd/TiO$_2$ to be the most effective catalyst for the dissociation reaction, but the least effective one for coupling of the CH$_x$ species. They have also observed increased dissociation with increasing temperatures (34).

The reaction studies as well as the NO decomposition experiments that we have reported earlier suggest that NO can decompose over both the metallic palladium and the palladium oxide and the major product is nitrous oxide. Over the reduced catalyst, in addition to nitrous oxide, some nitrogen is also produced. The reaction experiments presented in this article showed NO conversion levels of 10–12% when there was essentially no methane conversion, especially at the low temperature end, where the temperature was not high enough for the first hydrogen abstraction from methane.

Also seen in these results was the fact that the major product under these conditions was nitrous oxide, with selectivities around 60%. As the temperature increased, accompanied by increased methane conversion, the nitrous oxide formation rate went through a maximum and decreased as the nitrogen formation rate took over. Temperature programmed desorption experiment following NO adsorption and the temperature programmed oxidation using NO as the oxidizing agent gave only nitrous oxide (13), suggesting that NO coupling primarily leads to N_2O and that the N_2 formation requires the presence of CH_x species. Isotopic labeling experiments which involved switching from a mixture of $NO + CH_4 + O_2$ to $^{15}NO + CH_4 + O_2$ under steady state conditions showed very different surface residence times for species leading to N_2 or to N_2O, suggesting two different intermediates or possibly two different routes for the formation of these two products. These experiments also suggested the existence of a dimerized surface species residing on the surface for a long time and decomposing/desorbing to give N_2O. Existence of dimer-type species has been reported in the literature on various catalyst surfaces including Pd catalysts (36–41). Dimers are also shown to lead to N_2O formation over Ag catalysts (42). Dimers can be expected to be unstable at higher temperatures, subsequently resulting in a decrease in the selectivity to N_2O with increasing temperatures. In our oxygen exchange studies where we performed the switch $^{14}N^{16}O \rightarrow {}^{15}N^{18}O$ over the oxidized and the prereduced catalyst (32), doubly labeled or doubly unlabeled isotopes of nitrous oxide, such as $^{14}N_2O$, $^{15}N_2O$, $^{14}N_2{}^{18}O$, and $^{15}N_2{}^{18}O$, were formed, but there was no cross-labeled nitrous oxide species. This observation coupled with the fact that the transients for doubly unlabeled species relaxed very slowly suggests that N_2O formation goes through a stable dimeric intermediate and that these dimer-type intermediates can be formed on both oxidized and prereduced catalysts. We also suspect that the nitrous oxide observed under steady-state $NO-CH_4$ reaction conditions is also due to direct decomposition of NO through a dimeric intermediate.

It is highly probable that all three reactions, namely $NO + CH_4$ interaction, NO decomposition, and CH_4 combustion, take place on the catalyst surface simultaneously. To what extent each reaction takes place appears to be a strong function of the relative abundance of the oxidic or metallic palladium sites and the reaction medium. While the CH_4 combustion is the primary reaction over the oxidic sites, CH_x formation occurs primarily on the metallic palladium sites. CH_x species are essential for the reduction of NO to N_2. In the absence of CH_x species on the surface (e.g., at low temperatures, at higher space velocities, or over the oxide phase when CH_4 combustion becomes dominant) the direct decomposition of NO becomes important, leading to N_2O formation. When there is a sufficient concentration of CH_x species on the surface, however, the NO reduction to N_2 is the favored reaction. Based on the isotopic labeling studies we have performed (32), we also suspect that there may be a methyl dinitrosyl species acting as an intermediate and leading to the formation of N_2 and CO_2 as products of the same reaction step. We also envision that the direct combustion of methane on PdO sites leads to the formation of CO, which could oxidize further to CO_2 if there is sufficient oxygen available.

Based on this reaction scheme, it is possible to explain the occurrence of the product and reactant profile oscillations. The cyclic phase transformations that we suggest as the cause of these oscillations, on the other hand, can be explained by the thermodynamic equilibrium state of $PdO/Pd + O_2$ reaction that favors the metallic phase at higher temperatures and the highly exothermic nature of the CH_4 combustion reaction, which generates the temperature rise that drives the phase transformation toward the metallic phase. A more detailed discussion of these considerations is presented in a subsequent paper in these series (17).

One of the important observations in this study was the formation of ammonia in the high temperature range. Ammonia formation was observed in the presence as well as in the absence of oxygen in the gas phase. In general, its formation rate was seen to increase with temperature and decrease with increasing oxygen concentration. With the increase in temperature more methyl species are activated, leading to the formation of H(s) species on the surface which could possibly react with NO(ad) or even with N_2 which is the product. The formation of gas phase H_2 during these reactions cannot be ruled out either. The reaction of hydrogen with NO is much more heavily favored thermodynamically than its reaction with N_2, both being exothermic reactions (43). It is clear, however, that the concentration of NH_3 in the product stream is not determined by thermodynamic equilibrium.

No NO_2 formation was observed in our steady-state or transient response experiments. Although NO_2 is suggested as a possible intermediate in NO/CH_4 reaction in the literature (7, 44), all of these studies have reported essentially no activity in the absence of oxygen. The fact that we had very high NO reduction activity in the absence as well as in the presence of oxygen leads us to suspect that NO_2 is not a major intermediate in the reaction network over Pd/TiO_2 catalyst.

SUMMARY

The studies outlined in this article showed that Pd/TiO_2 catalysts can reduce NO in the absence as well as in the presence of oxygen. The reaction network is likely to include NO/CH_4 reaction, direct NO decomposition, and methane combustion. The extent of each of these reactions appears to be determined by the relative abundance of the oxidic

and metallic sites of palladium. The transformation of the sites between the two oxidation states seems to be very fast and driven by the temperature and the oxygen concentration in the medium. The results of our isotopic labeling studies performed under transient and steady-state conditions and a detailed analysis of the oscillatory behavior of the catalytic system are presented in the next two articles in this series (17, 32).

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