JOURNAL OF CATALYSIS **171,** 67–76 (1997)
ARTICLE NO. CA971793

Self-Sustained Oscillatory Behavior of $NO + CH_4 + O_2$ Reaction over Titania-Supported Pd Catalysts

Umit S. Ozkan,[1] Mahesh W. Kumthekar,[2] and Gurkan Karakas

Department of Chemical Engineering, The Ohio State University, 140 W. 19th Avenue, Columbus, Ohio 43210

Received September 9, 1996; revised June 16, 1997; accepted June 17, 1997

Self-sustained, regular oscillations were observed in $NO + CH_4 + O_2$ reaction over Pd/TiO_2 catalysts at specific temperatures and oxygen concentrations. The oscillatory behavior was investigated combining NO reduction and methane combustion reaction studies with additional catalyst characterization experiments performed under controlled atmospheres. The catalyst was prepared using a wet impregnation technique with Pd–acetate as the precursor for palladium. A fixed-bed, flow reactor system was used to perform the $NO + CH_4 + O_2$ and $CH_4 + O_2$ reaction experiments. Feed and product analyses were done on-line using gas chromatography–mass spectrometry, chemiluminescence, and wet chemistry techniques. Additional catalyst characterization was performed using thermal gravimetric analysis and high-temperature, controlled-atmosphere X-ray diffraction techniques. Detailed analysis of the oscillatory behavior has indicated that oscillations in the product and reactant profiles are coupled with temperature oscillations in the catalyst. When combined with controlled-atmosphere characterization experiments, these results, which can be reproduced in both $NO + CH_4 + O_2$ and $CH_4 + O_2$ systems, suggested that the oscillations are the result of periodic phase change of palladium on the surface. These cyclic phase transformations, in turn, are the result of temperature variations that are caused by the varying levels of exothermicity of the two major reactions, namely NO reduction and CH_4 combustion, that are favored by the metallic and the oxidic sites, respectively.

INTRODUCTION

In recent years much attention has been paid to the observation and analysis of oscillatory systems in chemistry, physics and biology. Detailed analysis of these systems provides us with some unusual insights into the mechanism of the physicochemical reactions occurring within the system. Several heterogeneous reactions have been reported to oscillate under specific conditions (1–6). In general, oscillatory behavior in heterogeneous systems has been poorly understood. Studying this behavior can provide information which could not be extracted from the analysis in the nonoscillatory mode.

Most of the heterogeneous catalytic reactions exhibiting oscillatory behavior involve oxygen participation and are exothermic in nature. Very often when these reactions oscillate, oscillations are also observed in the temperature of the catalyst surface. CO oxidation over Pt-based catalysts is probably the most widely studied heterogeneous catalytic reaction exhibiting oscillatory behavior (7–11). Nitric oxide reduction reactions with reducing agents such as hydrogen (12), ethylene (13), and propane (14) in the presence of oxygen have been reported to exhibit oscillatory behavior under certain conditions. The methane oxidation reaction has also exhibited oscillatory behavior over Pd catalysts (15).

In our previous studies, we have reported that NO could be effectively reduced by CH_4 over Pd/titania catalysts (16–18). In our more recent work we have investigated the effect of oxygen concentration and temperature on the kinetics of this reaction (19). We have also used isotopic tracers to investigate the mechanistic aspects of this reaction (20). The kinetics of the $NO-CH_4$ reaction were studied in the presence of oxygen at 500, 550, and 600°C. At each of these temperatures, above a certain critical oxygen concentration in the gas phase, regular, self-sustained oscillations were observed in the product and reactant profiles. Mass spectrometry was used in conjunction with different isotopes to separate products with similar *m*/*e* ratios to study these oscillations. In addition to the $NO + CH_4 + O_2$ reaction, we have observed oscillations in the $CH_4 + O_2$ reaction as well. In this paper we present findings from studies aimed at understanding the nature and the cause of this oscillatory behavior.

EXPERIMENTAL

Catalyst Preparation

The catalyst used in this study was 2 wt% Pd/TiO_2 which was prepared using a wet impregnation technique. The preparation has been described earlier (16). The TiO_2

---

[1] To whom correspondence should be addressed. Fax: (614) 292-3769. E-mail: ozkan.1@osu.edu.

[2] Present Address: Adv. Engineering Group, IMPCO/Air Sensors, 16804 Gridley Place, Cerritos, CA 90703-1741.

(anatase) (Aldrich) support was wet impregnated with a solution of Pd–acetate (Aldrich), with addition of oxalic acid to keep the pH at 4.0. The solution, which was stirred at 90°C for 4.5 h, was dried overnight at 100°C. The resulting catalyst was then calcined at 500°C for 5 h in oxygen. The resulting catalyst had a surface area of 12.0 m^2/g.

Catalyst Characterization

The catalyst used in this study was characterized using several techniques such as BET surface area measurements, scanning electron microscopy, laser Raman spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction, and thermal gravimetric analysis (TGA). The details of the catalyst characterization studies have been presented earlier (19).

Analysis of Oscillatory Behavior

The analysis of the oscillatory behavior in the NO–CH_4 reaction over a 2% Pd/TiO_2–anatase catalyst was performed using a flow reactor system discussed in detail earlier (19, 20). It consists of a feed system with mass flow controllers (Tylan model FC-280), a fixed-bed reactor, and a gas chromatograph–mass spectrometer (Hewlett–Packard 5890 GC-Hewlett–Packard 5989A MS engine). All the feed gases were mixed in a single stream prior to being sent to the reactor. The reaction experiments were carried out on a fixed bed of catalyst in a tubular reactor measuring 6.4 mm o.d. × 4.6 mm i.d. The catalyst loading was kept constant at 37.5 mg for different reactions. Quartz wool was placed at both ends of the catalyst bed to fix the solids in place. The temperature of the reactor was controlled by a PID controller (Omega CN 9111A). The effluent gases from the reactor were analyzed by bleeding a small amount through a blank capillary column into a gas chromatograph–mass spectrometer (GC–MS) (HP 5989 MS engine). The actual amount of effluent entering the MS detector was determined by the vacuum level inside the detector. The temperature of the MS source was kept at 100°C. The product analysis was carried out by using an on-line GC and on-line chemiluminescence NO_x analyzer (Thermo Environmental Instruments, Model 10). The reaction temperature was varied between 500 and 600°C. The NO and CH_4 concentrations were kept at 1780 ppm and 2.13%, respectively. The oxygen concentration was varied between 0 and 1.3%. Isotopes of reactants such as $^{13}CH_4$ and $^{15}N^{18}O$ were used to separate products with similar m/e ratios such as CO and N_2 with $m/e = 28$, and CO_2 and N_2O with $m/e = 44$. Temperature inside the catalyst bed during the oscillations was measured with a type K, grounded-junction thermocouple (Omega) with a diameter of 0.02 in. The time constant of the thermocouple is reported to be 0.2 s with water at room temperature. The temperature oscillations were recorded by a real-time, computerized data acquisition system.

Thermogravimetric Analysis

Thermogravimetric analysis was performed over this catalyst with two different temperature programs. In the first program, the catalyst was heated from room temperature to 1100°C at a rate of 20°C/min followed by an isothermal stretch at this temperature for 60 min. After the isothermal stretch the furnace was programmed to cool the catalyst to room temperature at a rate of 10°C/min. In the second temperature program, the catalyst was heated to 900°C at a rate of 20°C/min followed by an isothermal stretch at this temperature for 2 h after which the catalyst was cooled to room temperature at a rate of 10°C/min. These TGA experiments were performed in ambient air.

In thermogravimetric analysis, the weight and temperature of the catalyst were monitored with an ATI CAHN microbalance (Model TG-171) with a sensitivity of 1 μg and a B-type thermocouple, respectively.

Controlled-Atmosphere X-Ray Diffraction

High-temperature X-ray diffraction analysis was performed using an X-ray diffractometer (Scintag XDS-2000 equipped with a 0.85-liter controlled-atmosphere chamber and a platinum heating stage that could go up to 1600°C). The instrument had a Cu anode, 2-kW sealed-tube X-ray source, Θ-Θ goniometer, and a i-Ge solid state detector. The power used was 45 kV and 20 mA and the slits were set at 1 mm. The objective of this experiment was to verify the rapid transition between the Pd and PdO phases on the surface under a controlled environment. Pure PdO samples were obtained from Aldrich and used in this experiment without any further treatment. The heating stage was maintained at a constant temperature with the PdO sample on it. The sample chamber was filled with 1% O_2 (balance He) and a stream of this gas was constantly flushed through the sample chamber during the experiment. The intensity of the (101) reflection in PdO ($d = 2.644$ Å) was monitored as a function of time with 1% O_2 in the surrounding environment at three different temperatures, 500, 600, and 700°C. The PdO sample was maintained at the particular temperature for at least 30 min prior to the collection of data to ensure that an equilibrium has been achieved between the palladium sample and the gas phase oxygen.

RESULTS

Reaction Experiments

At 500°C complete NO conversion was obtained when CH_4 was used as a reducing agent in the absence of oxygen. Methane conversion was around 3.1% under these conditions. When the oxygen concentration was raised to 2100 ppm, still complete NO conversion was observed and the methane conversion increased to 7.1%. When the same reaction was investigated with the oxygen concentration of 2980 ppm, complete conversion for NO was observed and the methane conversion was seen to increase to 10.3%. When the oxygen concentration was increased to 3800 ppm the reaction exhibited self-sustained and regular oscillatory behavior in both reactant and product profiles. This experiment was repeated using ^{13}C-labeled methane to differentiate between different species which have the same *m*/*e* ratios. The oscillations obtained by monitoring the quadrupole signal for selected ions as a function of time are presented in Fig. 1. The amplitude of oscillations as a raw quadrupole signal is also indicated in Fig. 1. The methane conversion was seen to oscillate between 3 and 16%, while the NO conversion was seen to oscillate between 93 and 11%. The NO and CH_4 oscillations were observed to be out of phase with each other. The N_2 and N_2O signals were also out of phase with one another and the maxima for N_2 signal coincided with the minima for NO signal (i.e., maxima for NO conversion). The period of oscillations for all product and reactant concentrations were the same at about 23 s. Figure 2a shows three complete oscillation cycles of NO and CH_4 signals in superimposed form, clearly showing the minima in NO signal coinciding with the maxima in CH_4 signal. Figure 2b depicts the same three cycles for the CH_4 and N_2 signals, showing them to be in phase with each other, the implication being that the highest methane conversion coincides with the lowest N_2 yield.

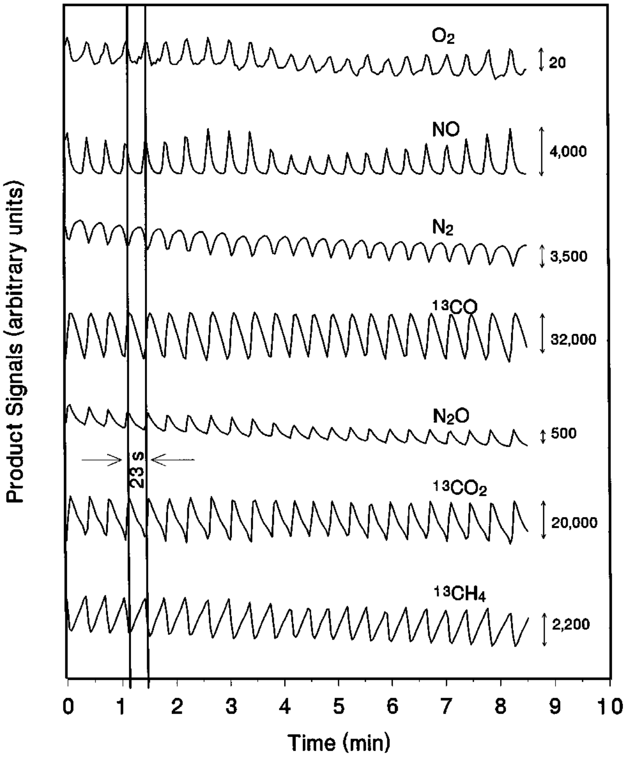

FIG. 1. Oscillations in reactant and product concentrations in the NO + CH_4 + O_2 reaction.

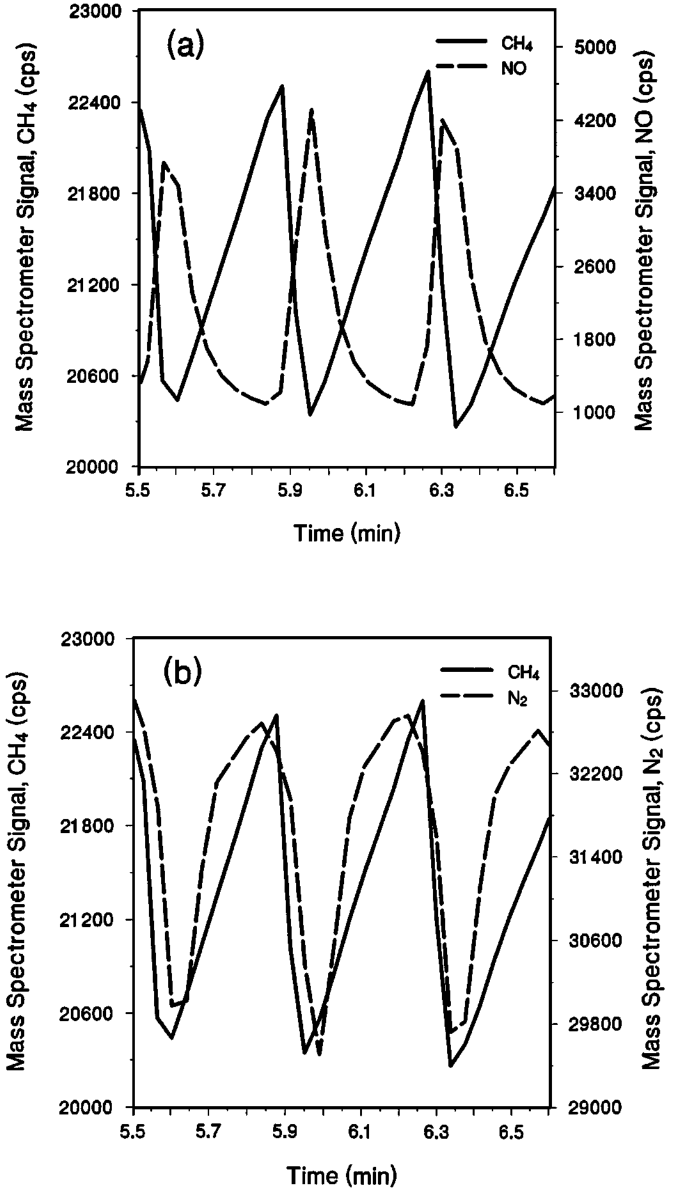

FIG. 2. Oscillations in (a) NO and CH_4 profiles and (b) N_2 and CH_4 profiles.

Keeping the same reactant concentrations that gave oscillations at 500°C, the temperature of the system was raised to 550°C. At this temperature, the oscillatory behavior disappeared giving a steady NO conversion approaching 100%. Increasing the oxygen concentration at this temperature to 8700 ppm again resulted in the oscillatory behavior of the catalyst. When the temperature was raised to 600°C, at the same oxygen concentration of 8700 ppm, the oscillations disappeared and the NO conversion went back to ~100%. A similar oscillatory behavior was exhibited by the catalyst at 600°C at 13,100 ppm of oxygen in the feed stream. The period of oscillations was seen to decrease with increasing temperature and oxygen partial pressure. A listing of

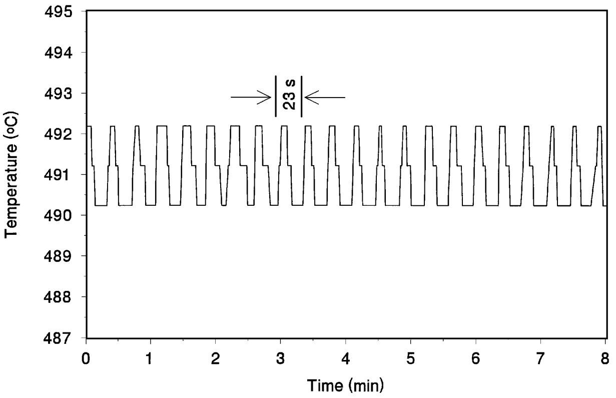

FIG. 3. Temperature oscillations in the $NO + CH_4 + O_2$ reaction.

the conditions under which oscillatory versus nonoscillatory behavior is observed is presented in Table 1. It summarizes the conversion data from different phases of this study, some of which have been presented earlier (19).

When the temperature of the catalyst bed was monitored by a thermocouple placed directly in the bed, the temperature of the catalyst was also seen to oscillate in synchronization with the oscillations observed in the concentrations of reactants and products (Fig. 3). The amplitude of temperature oscillations was 2°C. The maxima for temperature coincided with the minima in NO conversion and maxima in the CH_4 conversion. The period of oscillations was 23 s for temperature oscillations, similar to what was observed for concentration oscillations.

TABLE 1

Conditions for Oscillatory and Nonoscillatory Behavior of $NO + CH_4 + O_2$ Reaction

T (°C)	O_2 concentration (ppm)	% NO conversion	% CH_4 conversion
400	0	∼100	1.5
450	0	∼100	1.8
500	0	∼100	3.1
500	2100	∼100	7.1
500	2980	∼100	10.3
500	3800	Oscillations	
500	6500	Oscillations	
550	2100	∼100	9.7
550	2980	∼100	12.5
550	7000	∼100	20.9
550	8700	Oscillations	
600	2100	∼100	13.2
600	2980	∼100	13.6
600	7000	∼100	23.3
600	11725	∼100	36.7
600	13100	Oscillations	

At 500°C the oscillatory behavior was observed over a range of oxygen concentrations from 3800 to 6500 ppm. At an oxygen concentration of 7500 ppm, oscillations disappeared and the NO conversion remained steady at 10%. Methane conversion at this point was 17.5%. N_2O selectivity was seen to increase and the N_2 selectivity was seen to decrease in comparison to the selectivity values observed at oxygen concentrations that were lower than those that led to oscillations at the same temperature. A comparison of conversions and selectivities obtained below and above the oscillatory regime at 500°C is presented in Fig. 4.

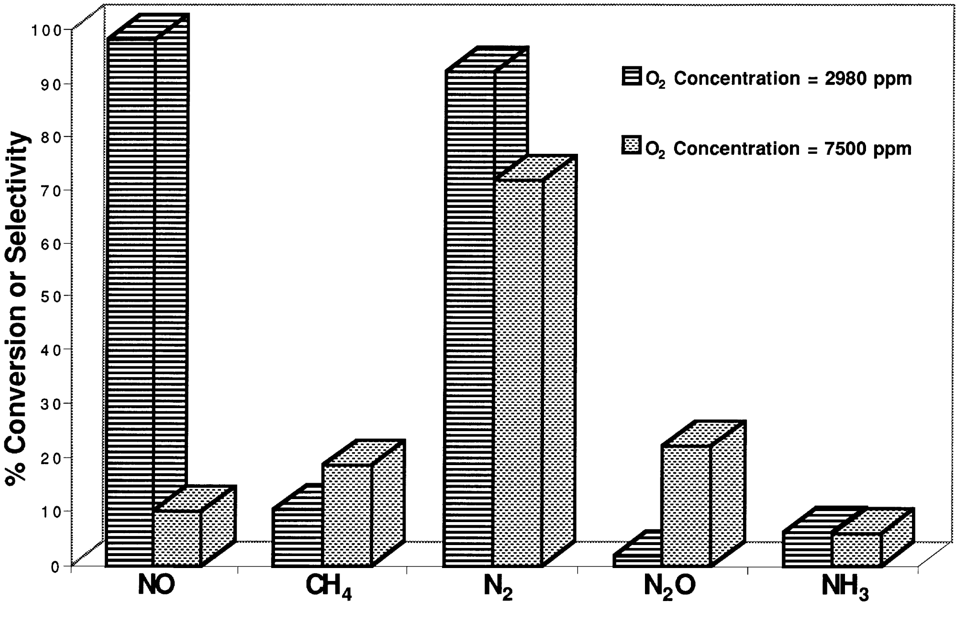

FIG. 4. Conversion and selectivities in the $NO + CH_4 + O_2$ reaction at O_2 concentrations below and above the oscillatory region.

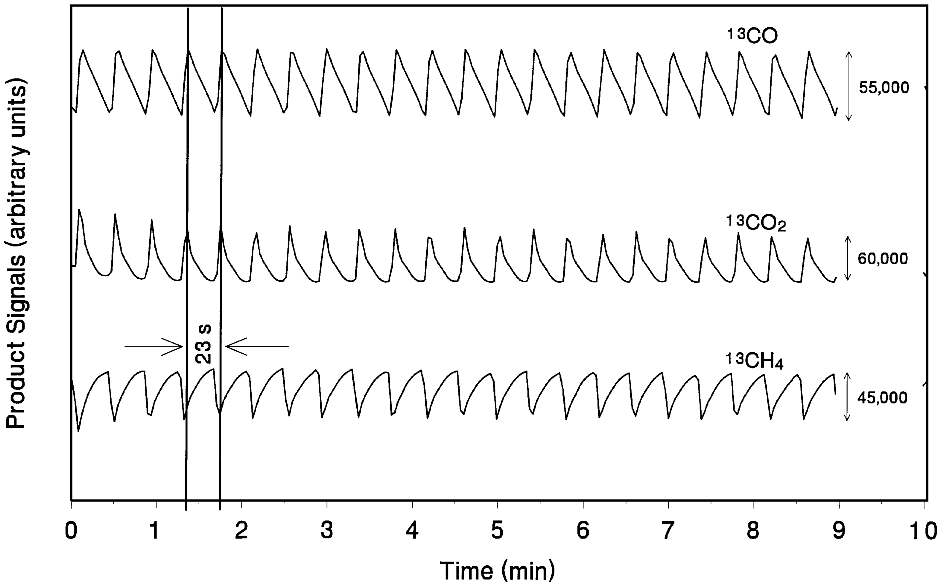

FIG. 5. Oscillations in reactant and product concentrations in the $CH_4 + O_2$ reaction.

Methane oxidation reaction experiments were also performed under identical conditions keeping CH_4 and O_2 concentrations at 2.13% and 3800 ppm, respectively, at 500°C. Similar self-sustained oscillations were observed in the methane oxidation reaction. The reactant and product profiles observed in this reaction are presented in Fig. 5. As expected, the CH_4 signal CO_2 signal are out of phase with each other. The methane conversion was seen to oscillate between 7 and 13%. When the catalyst bed temperature was monitored as a function of time, temperature oscillations of about 2.0°C were observed. These oscillations are presented in Fig. 6. The product oscillations and the temperature oscillations appeared to be in phase with each other. The period of oscillations for concentrations and for temperature was around 23 s. At 500°C, increasing the O_2 concentration to 7500 ppm took the system out of the oscillatory regime and gave a steady methane conversion of 18.8%.

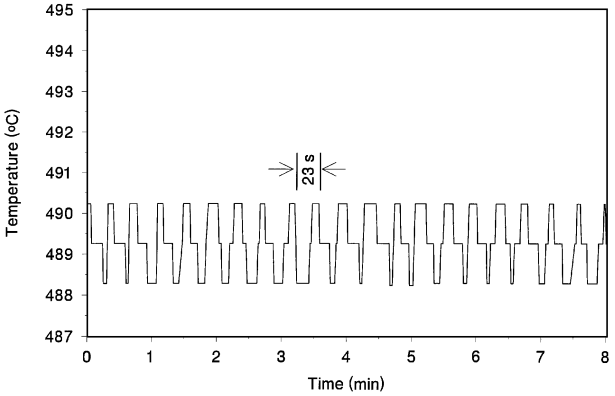

FIG. 6. Temperature oscillations in the $CH_4 + O_2$ reaction.

Thermogravimetric Analysis

Thermogravimetric analysis was performed on the oxidized Pd/TiO_2 catalyst with two different temperature programs. During the first temperature program, which involved increasing the temperature to 1100°C and keeping it at that level for 1 h followed by cooling to room temperature, it was observed that there was a sudden weight loss when the temperature of the catalyst reached around 875°C. The weight loss corresponded to the theoretical amount of oxygen associated with palladium oxide in the catalyst. During the isothermal stretch of the temperature program, the weight of the catalyst was seen to oscillate as shown in Fig. 7. The amplitude of these oscillations correspond to about 1.5% of Pd being reoxidized to PdO. When the temperature variation of the catalyst has been examined closely, similar oscillations were observed with amplitudes approaching 40°C. The period of oscillations for the weight and for the temperature was equal at 8.3 min. It was also observed that the maxima in temperature oscillations corresponded to the minima in weight oscillations. During the cooling phase when the temperature of 825°C was reached, the catalyst started gaining weight. By the end of the experiment when the catalyst was cooled to room temperature it had recovered 53% of the weight it had lost during the heating, pointing to a hysteresis effect.

When a similar experiment was performed with a different temperature program, which involved heating the catalyst to 900°C and keeping it at that temperature for 2 h followed by cooling to room temperature, a similar behavior was observed. The catalyst started losing weight at around 850°C, but when the catalyst weight reached its lowest point, the weight loss was equal to 53% of the theoretical

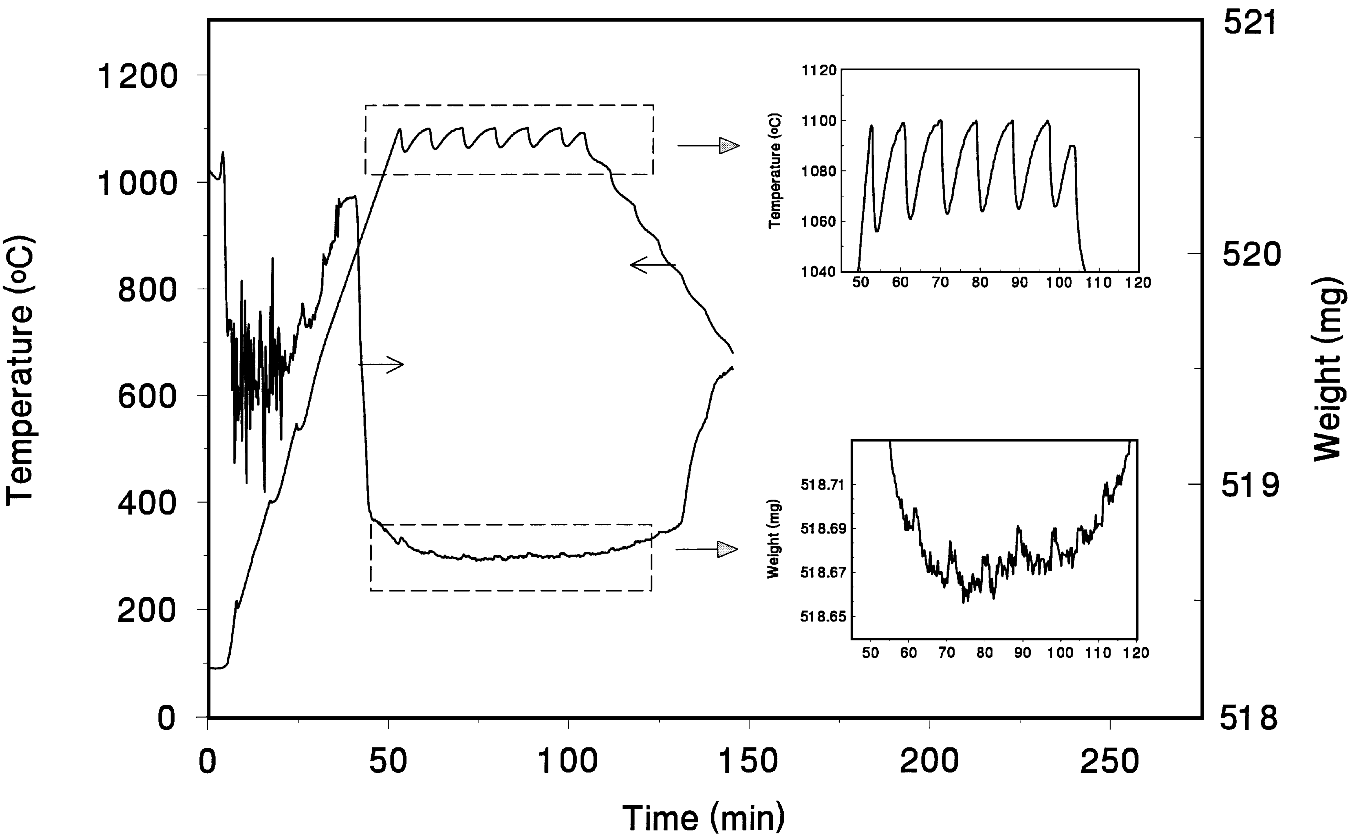

FIG. 7. Temperature and weight oscillations in the thermogravimetric analysis of Pd/TiO$_2$.

amount of oxygen in the PdO present, indicating only a partial reduction to Pd under this temperature program. During the 2-h isothermal stretch at 900°C, oscillations were observed in the weight of the catalyst with amplitudes that corresponded to 6.5% of total palladium oxidizing back to PdO. Catalyst temperature was also seen to exhibit oscillations of about 10°C. The period of these oscillations was 9 min.

High-Temperature Controlled-Atmosphere X-Ray Diffraction

In order to obtain a direct evidence of the phase transformation between Pd and PdO, we performed X-ray diffraction analysis of the catalyst in a controlled environment. A sample of palladium oxide was maintained at 500°C on a heating stage in an atmosphere of 1% O$_2$ with balance helium. The intensity of the (101) reflection, which is the most intense peak in the X-ray diffraction pattern of PdO, was monitored under these conditions as a function of time. The variation of the signal is presented in Fig. 8. The data were processed using Savitzky–Golay data smoothing technique, which involved using a nine-point least square method with 602 of the output points (21). The signal smoothed through the Savitsky–Golay mathematical manipulation is also presented in Fig. 8. As can be seen from both the unprocessed signal and processed signal, the intensity of the (101) reflection oscillates with time. The high temperatures used cause loss of signal due to high levels of noise; nevertheless, the oscillatory behavior is evident even in the unprocessed signal. The period of these oscillations was around 6 min. The oscillatory behavior of the intensity of (101) reflection was observed at all three temperatures, namely, 500, 600, and 700°C, investigated. There was a decrease in the period with increasing temperature. The signal also became weaker and noisier with increasing temperature.

DISCUSSION

In our previous articles (16–20), we presented the activity of Pd/TiO$_2$ catalyst for the reduction of NO with methane in the absence as well as in the presence of oxygen. The previous results led us to suggest that the three independent reactions, namely, NO reduction with CH$_4$, NO decomposition, and CH$_4$ combustion, make up the major components of a multireaction network on the surface of Pd/TiO$_2$ catalysts and the extent of each of these reactions is dictated by the relative abundance of the metallic and the oxidic sites of palladium.

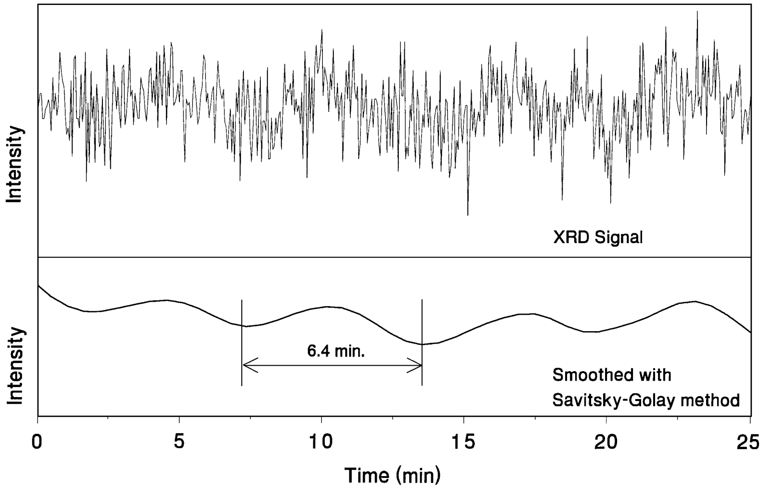

FIG. 8. Oscillations in the (101) X-ray diffraction signal of PdO at 500°C.

$$4NO + CH_4 \rightarrow 2N_2 + 2H_2O + CO_2 \qquad [1]$$

$$2NO \rightarrow N_2 + O_2 \qquad [2]$$

$$2NO \rightarrow N_2O + 1/2O_2 \qquad [3]$$

$$CH_4 + O_2 \rightarrow CO_2 + H_2O. \qquad [4]$$

We proposed that the metallic sites are active for the formation of CH_x species whereas the oxidic sites lead to direct methane combustion. According to the reaction scheme we proposed, reduction of NO to N_2 takes place also on the metallic sites, possibly through the formation of a methyl dinitrosyl type intermediate from the interaction of surface CH_x groups with NO molecules.

$$[CH_x\text{–}NO\text{–}NO]^*_{(s)} \rightarrow N_2 + CO_2 + xH_{(s)}. \qquad [5]$$

N_2O observed in our studies, on the other hand, is primarily a result of direct NO decomposition through a stable, dimerized intermediate, which could be formed over both oxidized and reduced sites.

$$(NO)_{2(s)} \rightarrow N_2O_{(g)} + O_{(s)} \qquad [6]$$

Although further decomposition of N_2O to N_2 over reduced sites remains as a possible path, it does not appear to contribute to the N_2 formation to any significant extent in the presence of CH_x species. The transient experiments performed using isotopic labeling studies, which showed the surface residence times to be significantly longer for the intermediates leading to N_2O formation than for those leading to N_2 formation provided additional support to the proposed reaction network (20). We reported that the $NO + CH_4 + O_2$ system showed self-sustained oscillatory behavior when the oxygen concentration was raised to a certain critical level at each temperature and that this level increased with oxygen concentration. We suggested that the oscillations were the result of cyclic phase transformation of Pd on the surface between the oxide and the metal. In this article, we report the use of this oscillatory behavior as a probe to examine the catalytic functionality of the metallic and oxidic sites and the reaction network.

Periodic phase changes of catalysts have been established as the cause of oscillatory behavior in several reaction systems (22, 23), including reactions over Pd-based catalysts (24–28). Amariglio *et al.* (22) described oscillatory behavior in propene oxidation over copper oxides at low conversion levels. They argued that the formation of CO_2, which is much more exothermic and oxygen consuming than that of acrolein, is favored on CuO and causes a temperature increase in the solid. Reducing conditions are thus created leading to Cu_2O formation. On Cu_2O, acrolein formation, which is less oxygen consuming, is favored and it leads to a decrease in the temperature. Lower temperatures, in turn, facilitate the reoxidation of the solid. This process is repeated giving the oscillatory behavior. Kurtanjek *et al.* (23), who studied hydrogen oxidation over a nickel catalyst, also reported oscillatory behavior and through the use of contact potential difference (CPD) measurements showed the Ni catalyst to oscillate between reduced and oxidized states, giving rise to oscillations in product concentrations. Similar conclusions were drawn by Rajagopalan *et al.* (24), who also studied hydrogen oxidation over palladium wires. Konig *et al.* (15) reported oscillatory behavior in the product and reactant profiles in methane oxidation over thick Pd/PdO films at 500°C with 4% CH_4 and 2% O_2 in the feed stream. Using the ellipsometric technique, they concluded that the oxidation state of palladium was changing from PdO to metallic Pd. These conclusions were backed by visual observations that the color of the catalyst changed from brownish to gray which corresponds to PdO and metallic Pd, respectively. Jaeger and co-workers (25–28) studied CO oxidation on highly dispersed Pd embedded in a zeolite matrix. Periodic oscillations observed in this case were explained in terms of the surface palladium going from metallic Pd (Pd^0) to PdO (Pd^{2+}).

In this study, when the oscillatory behavior of the $CH_4 + NO + O_2$ reaction is examined in detail using ^{13}C-labeled methane, one of the most significant features observed is that the oscillations for the two reactants, i.e., NO and CH_4, are 180° out of phase with one another (Figs. 1 and 2). N_2 and CH_4 signals, on the other hand, are completely in phase with each other, implying that the highest methane conversion coincides with the lowest N_2 yield. This is possibly one of the best pieces of evidence that the catalyst is not simply behaving as a "nonselective" methane combustion catalyst, but that there are distinct routes and distinct sites for NO reduction and methane combustion reactions. Otherwise, one would expect to get the highest methane conversion also leading to the highest NO conversion. Also interesting is the fact that N_2 and N_2O are 180° out of phase with each other, the maxima for N_2O corresponding to the minima in NO conversion, which in turn, coincides with the maxima in CH_4 conversion. This observation is in perfect agreement with our earlier results which suggested different intermediates and different routes for the formation of N_2 and N_2O (20). When the reactant and product concentration oscillations are analyzed simultaneously with the temperature oscillations, we see that the temperature maxima correspond to CH_4 conversion maxima as well as N_2O concentration maxima. Since, at any given oxygen concentration, higher temperatures favor the formation of (Pd^0) sites, it is conceivable that the oscillations are the results of periodic transformations between the metallic and the oxidic phases on the surface. The observations made in the oscillatory regime are consistent with the proposed reaction scheme, which assigns the methane combustion and N_2O formation through direct decomposition of NO to the oxidic sites and the CH_x formation and NO reduction to the metallic sites. The fact that the CH_4 conversion does not go to zero at the minima also supports our earlier suggestion that the role of methane is not simply a reduction of the surface following decomposition of NO, but that it is directly involved in the reduction of NO through the formation of a common intermediate which leads to N_2 formation.

Another interesting point to note about the reactant and product oscillations is that while the CO oscillations seem to be smooth and symmetrical, the oscillations for CO_2 and CH_4 exhibit a skewed nature with a shoulder-like feature appearing to the right and to the left of the maxima for the two species, respectively. Since the CH_4 and CO_2 concentration oscillations are out of phase with each other, it is evident that the shoulder-like feature appears on the "reducing half" of the cycle (i.e., transition from PdO to Pd) for both species. This behavior suggests that the formation of CO is likely to result from a single reaction associated with a single phase, whereas the rise and fall of CO_2 and CH_4 signals are dictated by double reactions which involve both of the phases. This observation is also consistent with our reaction scheme, which suggests that CO is formed as a first step in direct CH_4 oxidation on oxidic sites, but the CO_2 formation can be the result of two different reactions taking place on two different phases, namely, the decomposition of a methyl dinitrosyl-type species over the metal phase and further oxidation of CO over the oxide phase. Similarly, CH_4 conversion is also tied to two different reactions, namely, formation of CH_x species on the metallic sites and direct oxidation of methane over the oxidic sites. In the presence of NO, the surface CH_x groups are envisioned to take part directly in the NO reduction step, forming N_2.

The fact that the methane combustion reaction also showed oscillations which were accompanied by temperature oscillations and that the temperature maxima coincided with methane conversion maxima provides evidence that the oscillations observed in $NO + CH_4 + O_2$ reaction are not specific to the reaction system, but are specific to the catalyst used.

The results obtained when we examined the behavior of the catalyst below and above the oscillation regime by keeping all parameters the same, and changing only the oxygen concentration, provided some complementary evidence to the proposed reaction scheme. At 500°C, oxygen concentrations of 0 to 3800 ppm gave essentially complete NO conversion, with N_2 selectivities over 90%. When the oxygen concentration was raised above 3800 ppm, oscillations were observed. The oscillatory regime covered the oxygen concentrations ranging from 3800 to 7500 ppm. When the oxygen concentration was raised to 7500 ppm, the oscillations disappeared. However, the steady-state conversion level for NO dropped to 10%, and CH_4 conversion increased, as expected. More interestingly, the selectivity for N_2 decreased compared to its "below oscillation regime" value and N_2O selectivity increased, reinforcing the previous conclusions. Additional control experiments we performed involved a comparison of the behavior of fully oxidized and prereduced catalysts during the first 20 min of the $NO + CH_4 + O_2$ reaction using parameters that fell below the oscillatory regime (20). Over the oxidized catalyst, the NO reduction rate started out very low and increased with time. The CH_4 conversion rate, on the other hand, started out quite high and leveled off with time. During the first few minutes of the reaction, significant levels of N_2O were also observed which decreased to negligible levels as time went on. The behavior of the oxidized catalyst became identical to that of the prereduced catalyst within 20 min, supporting the catalytic functions assigned to the oxide and metal phases in the proposed scheme.

The phase transformation between metallic Pd and PdO has been reported in the literature in detail (29, 30). These studies point to the equilibrium between Pd and PdO phases that is readily attainable. Equilibrium calculations performed using Gibbs free energy estimations (31) predict decomposition temperatures that range from 400°C at 300 ppm O_2 to 700°C at 14% O_2 (32). Although the oxygen concentrations which induced oscillations at each temperature were lower than the oxygen concentration predicted for the $PdO/Pd + O_2$ equilibrium at each temperature, this difference can be due to support effects which may render the decomposition behavior of PdO dispersed on the surface quite different from that of the bulk PdO. The temperature-programmed desorption and reduction experiments, which hinted at the increased oxygen mobility of the titania support when Pd is supported on it, are consistent with this observation and can help explain why oscillations start at lower oxygen concentrations than predicted.

When the exothermicity of these reactions are examined, we see that although both $NO + CH_4 + O_2$ and $CH_4 + O_2$ reactions are highly exothermic, however, the extent of the direct combustion reaction is much higher over the oxide phase, leading to the observed temperature rise, which is sufficient to convert the oxide on the surface to the metallic phase. The heat of reaction calculations has shown that the heat generated in the reducing half of the cycle is sufficient to convert 55% of PdO on the surface to Pd (32).

The TGA experiments have provided additional evidence of the rapid phase changes of palladium on the surface even in the absence of reactants. In agreement with earlier reports in the literature (28, 29), PdO on the surface was observed to lose all its oxygen around 825°C, as evidenced by the corresponding weight loss of the catalyst. During the isothermal stretch that followed the weight loss, oscillations were observed in the weight of the catalyst and the oscillations in weight were seen to accompany oscillations in temperature. Since the temperature maxima correspond to weight minima, these oscillations cannot be explained by buoyancy effects. It is conceivable that the oscillations in this case are triggered by the exothermicity of the oxidation reaction of palladium, which can result in local temperature variations large enough to shift the Pd/PdO equilibrium in the reverse direction. It should also be noted that the amplitude of the temperature oscillations is too large to be induced solely by the heat of reaction effects and we believe that temperature oscillations are accentuated by the temperature controller of the furnace. However, it is clear that the temperature oscillations are triggered spontaneously and these oscillations are accompanied by weight oscillations. Similar oscillations have been reproduced at a lower temperature (900°C) with a smaller amplitude in temperature oscillations.

Another interesting observation from the TGA experiments has been the "hysteresis" behavior of the Pd/PdO conversion. When the temperature has been lowered to room temperature, the catalyst was seen to gain only about 53% of its initial weight loss. This observation is similar to what has been earlier reported in the literature for Pd/PdO transition (29).

Possibly the most direct evidence of the rapidity of Pd/PdO transition in this study has been obtained through the controlled-atmosphere, high-temperature X-ray diffraction analysis. At 500, 600, and 700°C in 1% oxygen concentration, distinct oscillations were seen in the intensity of (101) reflection of PdO indicating that in 1% O_2 atmosphere 500°C was high enough to drive at least some of the surface palladium into a cycle of phase transition between the oxidic and metallic phases. It should be noted that in order to observe the change in the intensity of the (101) reflection of PdO, one should have at least some partial phase change in the bulk (i.e., long-range ordering). If one can have the partial phase transition in the bulk, one would expect to achieve a surface transition between the oxide and the metallic phases much more readily.

The fact that similar oscillations in the intensity of (101) reflection were observed even at two higher temperatures for the same oxygen concentration indicates that for every O_2 concentration there is a range of temperatures which will be sufficient for inducing the cyclic behavior between phases. The decreasing amplitude of oscillations with increasing temperature is also consistent with the fact that the higher temperatures would drive the Pd/PdO equilibrium toward the metallic phase and hence reduce the intensity of the characteristic (101) reflection of palladium oxide.

CONCLUSIONS

The results described in this article combined with the isotopic labeling and characterization studies presented in previous publications lead us to conclude that the oscillations observed in the $NO + CH_4 + O_2$ reaction under certain reaction conditions are the result of cyclic phase transformation of palladium between the metallic and the oxidic phases. It is possible to generate these cyclic phase transformations during $NO + CH_4 + O_2$ and $CH_4 + O_2$ reactions as well as in the presence of oxygen without any reducing agent being present. At every temperature there is an oxygen concentration range below and above which the catalyst surface is stable in the metallic phase and the oxidic phase, respectively. In between, however, there is an oscillatory regime where the thermodynamic equilibrium for Pd/PdO system is shifted back and forth. These shifts are triggered by the local temperature changes in the catalyst due to the exothermic nature of the reactions, examples of which include $NO + CH_4$ reaction, CH_4 oxidation, and even Pd oxidation.

The catalytic implications of this behavior in the NO reduction system that we are focusing on are such that the system oscillates between two groups of reaction. On the reduced phase, the dominant reaction is NO reduction to N_2 by CH_4. On the oxidized phase, the dominant reaction is direct methane oxidation. Although direct NO decomposition could take place on both phases, our results lead us to conclude that N_2O formation mainly occurs on the oxidic phase through direct NO decomposition. At oxygen concentrations that fall below or at temperatures that fall above the oscillatory regime, the catalyst is capable of reducing NO with CH_4 with NO conversion levels approaching 100% and N_2 selectivities approaching 95%. The exact boundaries for the oscillatory region will depend on not only the gas phase oxygen concentration and temperature, but also on the type of reactions taking place on the surface, the presence of other gas phase species, and the nature of the support material.

ACKNOWLEDGMENT

The financial support provided for this work from National Science Foundation through Grant CTS-9412544 and from Exxon Foundation is gratefully acknowledged.

REFERENCES

1. Sharma, S., Boecker, D., Maclay, G. J., and Gonzalez, R. D., *J. Catal.* **110**, 103 (1988).
2. Eng, D., Stoukides, M., and McNally, T., *J. Catal.* **106**, 342 (1987).
3. Abdul-Kareem, H. K., Silverston, P. L., and Hudgins, R. R., *Chem. Eng. Sci.* **35**, 2077 (1980).
4. Eiswirth, M., Moller, P., and Ertl, G., *Surf. Sci.* **208**, 13 (1989).
5. Flytzani-Stephanopoulos, M., Schmidt, L. D., and Caretta, *J. Catal.* **64**, 346 (1980).
6. Vayenas, C. G., Lee, B., and Michaels, J., *J. Catal.* **66**, 36 (1980).
7. Barkowski, D., Haul, R., and Kretschmer, U., *Surf. Sci.* **107**, L329 (1981).
8. Kapicka, J., and Marek, J., *J. Catal.* **119**, 508 (1989).
9. Shanks, B. H., and Bailey, J. E., *J. Catal.* **110**, 197 (1988).
10. Imbihl, R., Ladas, S., and Ertl, G., *Surf. Sci.* **215**, L307 (1989).
11. Yeates, R. C., Turner, J. E., Gellman, A. J., and Somorjai, G. A., *Surf. Sci.* **149**, 175 (1985).
12. Janssen, N. M. H., Cobden, P. D., Nieuwenhuys, B. E., Ikai, M., and Tanaka, K., "14th North American Meeting of The Catalysis Society, 1995," Technical Program Abstracts, T-22.
13. Cho, B. K., Yie, J. E., and Rahmoeller, K. M., "14th North American Meeting of The Catalysis Society, 1995," Technical Program Abstracts, T-64.
14. Halasz, I., Brenner, A., Ng, K. Y., and Shelef, M., "14th North American Meeting of The Catalysis Society, 1995," Technical Program Abstracts, T-63.
15. Konig, D., Weber, W. H., Poindexter, B. D., McBride, J. R., Graham, G. W., and Otto, K., *Catal. Lett.* **29**, 329 (1994).
16. Kumthekar, M. W., and Ozkan, U. S., *Catal. Today* **35**, 107 (1997).
17. Kumthekar, M. W., and Ozkan, U. S., *Appl. Catal. A: Gen.* **151**(1), 289 (1997).
18. Ozkan, U. S., Kumthekar, M. W., and Mitome, J., *Catal. Today*. [accepted for publication]
19. Kumthekar, M. W., and Ozkan, U. S., *J. Catal.* **171**, 45 (1997).
20. Kumthekar, M. W., and Ozkan, U. S., *J. Catal.* **171**, 54 (1997).
21. Savitzky, A., and Golay, M. J. E., *Anal. Chem.* **36**, 1627 (1964).
22. Amariglio, A., Benali, O., and Amariglio, H., *J. Catal.* **118**, 164 (1989).
23. Kurtanjek, Z., Sheintuch, M., and Luss, D., *J. Catal.* **66**, 11 (1980).
24. Rajagopalan, K., Sheintuch, M., and Luss, D., *Chem. Eng. Commun.* **7**, 335 (1980).
25. Svensson, P., Plath, P. J., and Jaeger, N. I., "Proceedings, VIth International Symposium on Heterogeneous Catalysis, Sofia, 1987," p. 13.
26. Svensson, P., Jaeger, N. I., and Plath, P. J., *J. Phys. Chem.* **92**, 1882 (1988).
27. Jaeger, N. I., Moller, K., and Plath, P. J., *J. Chem. Soc., Faraday Trans.* **82**, 3315 (1986).
28. Slin'ko, M. M., Jaeger, N. I., and Svensson, P., *J. Catal.* **118**, 349 (1989).
29. Farrauto, R. J., Hobson, M. C., Kennelly, T., and Watermann, E. M., *Appl. Catal. A: Gen.* **81**, 227 (1992).
30. Rodriguez, N. M., Oh, S. G., Dalla-Betta, R. A., and Baker, R. T. K., *J. Catal.* **157**, 676 (1995).
31. Mallika, C., Sreedharan, O. M., and Gnanamoorthy, J. B., *J. Less-Common Metals* **95**, 213 (1983).
32. Kumthekar, M. W., Ph.D. Dissertation, Ohio State University, 1996.