ELSEVIER

Catalysis Today 53 (1999) 597–606

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Role of lanthanide elements on the catalytic behavior of supported Pd catalysts in the reduction of NO with methane

Junko Mitome, Enrique Aceves, Umit S. Ozkan *

Department of Chemical Engineering, The Ohio State University, Columbus, OH 43210, USA

Abstract

In this study, the role of lanthanide elements (Ce, Gd, La, and Yb) on Pd/TiO_2 catalysts in the catalytic reduction of NO with methane was investigated. Steady-state reaction experiments in the presence of oxygen showed that the addition of lanthanide elements increases the oxygen resistance of the catalyst. The post-reaction XPS characterization results revealed that majority of the Pd sites remained in the zero oxidation state in the presence of Ce or Gd. The effect of SO_2 (145 ppm) and H_2O (0–6.6%) in NO–CH_4–O_2 reaction over supported Pd and Gd–Pd catalysts was also investigated. Over the Gd–Pd catalyst with the presence of SO_2, more than 70% NO conversion was obtained for over 6 h while the Pd only catalyst showed a sharper drop in NO conversion. Over the Gd–Pd catalyst, the presence of H_2O showed no effect on NO conversion activity (>99% conversion) during the 18 h the catalyst was kept on stream. Among the lanthanide elements tested, Gd is the most effective, allowing the use of above stoichiometric oxygen concentration. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: NO reduction; Methane; Palladium; SO_2; Sol-gel; Lanthanide

1. Introduction

Nitric oxide reduction with hydrocarbons has recently attracted much attention due to stricter environmental regulations. Especially, using methane as a reducing agent has certain advantages since it is the least expensive lower hydrocarbon and exists abundantly in natural gas. There have been numerous studies in the literature on NO reduction over ZSM-5 supported catalysts using hydrocarbons including methane. A review on NO reduction by methane over many zeolite supported catalysts can be found in Ref. [1].

In some studies, precious metals such as palladium were incorporated into the zeolite using the ion exchange method. Pd^{2+} exchanged H-ZSM-5 and Pd–H–Ce–ZSM-5 displayed considerable activity for NO reduction using methane in the presence of oxygen. Acidity was essential for this reaction [2].

Any good SCR catalyst needs to be able to work effectively in oxygen rich environment. Ceria is widely recognized as a type of oxygen scavenging material. A large volume of studies on three-way catalysts can be found in the literature. NO + CO reaction over alumina supported rhodium catalysts doped with ceria or ceria supported rhodium catalysts was studied extensively [3,4,5,6]. Further, alumina or ceria supported platinum [7,8] along with Pt–Rh bimetallic particles [9] have also been studied. Muraki et al. [10] studied the effect of La_2O_3 in the NO reduction over alumina supported palladium catalysts and found that the addition of La_2O_3 improved the reduction activity. Using the interaction between Pd and Ce, new catalyst designs have been developed [11].

---

* Corresponding author. Tel.: +614-292-6623; fax: +614-292-3769

E-mail address: ozkan.1@osu.edu (U.S. Ozkan)

0920-5861/99/$ – see front matter ©1999 Elsevier Science B.V. All rights reserved.

PII: S0920-5861(99)00147-9

Recently, many SCR researchers have also focused on the use of ceria. Zhang and Stephanopoulos investigated the effect of the addition of Ce(II) ions on the activity and hydrothermal stability Cu–ZSM-5 for NO decomposition. They found that the presence of cerium suppressed CuO particle formation and dealumination, providing higher hydrothermal stability for the zeolite structure and higher copper dispersion [12].

Along with the reaction/mechanistic studies, thermodynamic properties of cerium and lanthanum compounds containing oxygen and sulfur have been studied by Kay et al. [13]. Characterization of Pt/γ–alumina containing ceria has been extensively studied by Shyu et al. [14,15] which provides insight to the effect of Pd and Pt on the reduction/oxidation of ceria.

In an effort to improve the oxygen storage/transport characteristics, Cho [16] has incorporated gadolinia onto a commercial ceria powder. Dziewiecka et al. [17] studied NO reduction with hydrocarbons over a series of copper–gadolinia oxide catalysts supported on thermal resistant carriers. They both found that NO reduction activity was increased by the presence of gadolinia.

Previously, we have investigated a palladium-based catalytic system in reducing NO with CH_4. $Pd/TiO_2$was found to give 100% NO conversion to N_2 with over 95% selectivity at GHSV >70,000 h^{-1}. The main observations from these earlier studies were that it was possible to completely convert NO with methane with or without gas phase oxygen being present in the feed. We also concluded that NO–CH_4 reaction, direct NO composition, and direct methane combustion were likely to take place on the surface simultaneously and the extent of each reaction was a strong function of the oxidation state of Pd and of the reaction parameters. It was also concluded that metallic palladium sites were needed to selectively reduce NO to N_2 and the transition between the Pd and PdO phases was relatively easy and rapid under reaction conditions [18]. In the subsequent publications, we have presented the results regarding the mechanistic aspects of NO–CH_4 interaction using the isotopic labeling studies. Based on these results, it was concluded that N_2 is formed through direct participation of CH_4 whereas N_2O formation is mainly a result of NO decomposition reaction. It was also observed that at least three types of reactions occur simultaneously on the surface, namely NO + CH_4, CH_4 oxidation and NO decomposition. The extent of these reactions is determined by the oxidation state of palladium on the surface [19]. In the NO + CH_4 + O_2 reaction studies, we have observed self-sustained, regular oscillations 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. It was found 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 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 [20]. All of these studies were done using dry feed. Our more recent work includes the investigation of the water vapor effect over the Pd/TiO_2 catalyst. The catalyst did not lose its activity and maintained 100% NO conversion with 6% water vapor in the feed with the presence of oxygen for over 24 h demonstrating the high hydrothermal stability of the catalyst [21]. In this study, our catalysts were modified using lanthanide metals such as Ce, Gd, La, and Yb in an effort to increase the oxygen tolerance. Steady-state reaction experiments were performed in the presence of O_2, H_2O, and SO_2. Pre- and post-reaction characterization of the catalysts were done using a controlled-atmosphere X-ray photoelectron spectroscopy technique.

2. Experimental

2.1. Catalyst preparation

The catalysts used in this study, 1% Ce/TiO_2, 2% Pd/TiO_2, 1% Ce/2% Pd/TiO_2, and 1% Gd/2% Pd/TiO_2, were prepared by a wet impregnation technique and a modified sol–gel method. Precursors utilized were palladium acetate, titanium (IV) oxide, cerium nitrate, gadolinium nitrate, titanium (IV) isopropoxide, all obtained from Aldrich. Palladium acetate and cerium nitrate were impregnated into an acetone solution containing titanium (IV) oxide. The solution was dried over night with agitation followed by calcination under oxygen at 500°C for 4 h with heating and cooling rates of 10°C/min. In a modified sol–gel method, palladium acetate was dissolved completely in isopropyl alcohol followed by addition of titanium (IV) isopropoxide. The titanium precursor was hydrolyzed dropwise by an aqueous solution containing gadolinium nitrate. The solution was dried over night with stirring under ambient conditions followed by calcination under oxygen at 500°C for 4 h with heating and cooling rates of 4.5°C/min. The BET surface areas of these catalysts were measured using nitrogen adsorption to be 19, 12, and 79 m^2/g for 2% Pd/TiO_2, 1% Ce/2% Pd/TiO_2, and 1% Gd/2% Pd/TiO_2, respectively.

2.2. *Catalyst characterization*

Surface characterization techniques used in this study included X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), BET surface area measurements. The controlled-atmosphere X-ray photoelectron spectra of reduced and post-reaction samples were obtained by a Physical Electronics/Perkin–Elmer (Model 550) ESCA/Auger spectrometer, operated at 15 kV and 20 mA. Al K_α radiation ($h\nu = 1486.6$ eV) was used as the X-ray source. The charge shift was corrected using the binding energy of C 1*s* (284.6 eV) as a reference.

TPD experiments were carried out using a home-made TPD set up which is capable of in situ calcination and reduction. Desorption species were detected by a quadruple mass spectrometer (5989A HP). All samples were pretreated with oxygen at 500°C for 2 h followed by reduction at 200°C by a mixture of 33% H_2 in He for 2 h before an adsorbate was introduced. Samples were heated at 10°C/min from room temperature to 700°C.

2.3. *Reaction studies*

The steady-state reaction experiments were performed using a fixed-bed flow reactor (1/4 in. O.D.) made of stainless steel. The amount of catalyst packed was varied between 37.5 and 69 mg. The feed composition consisted of NO (500–1780 ppm), CH_4 (1.065–2.13%), O_2 (0.1–4.3%), SO_2 (0–145 ppm), and H_2O (0–7%) in balance He at flow rates between 30 and 61 cm^3(STP)/min. The reaction temperature was varied between 400° and 500°C which was controlled by a PID temperature controller (Omega). In each reaction, the sample was pre-reduced using a mixture of 33% H_2 in He at 200°C for 30 min. The system was facilitated with a syringe pump to accommodate the water injection during steady-state reaction experiments. All lines were heated at 136°C to prevent the condensation of water. The feed and effluent were analyzed on-line using a combination of a gas chromatograph (5890A HP), a chemiluminescnece NO–NO_2–NO_x analyzer (Themo Environmental Instruments, Model 42H), and an IR ammonia analyzer (Siemens Ultramat 5F). The gas chromatograph was equipped with a 10 ft × 1/8 in. Porapaq Q column and a 8 ft × 1/8 in. molecular sieve column to quantify N_2, O_2, CO, CO_2, CH_4, N_2O, and SO_2. In all experiments, nitrogen and carbon balances were close to 100%.

3. Results and discussion

3.1. *Effect of Ce and Gd*

As we reported in previous papers [18–20], the 2% Pd/TiO_2 catalyst was effective in reducing NO by methane in the presence of O_2. However, at a certain O_2 concentration and at each temperature level, self-induced oscillations in feed and product were observed [20]. To eliminate the oscillations, we have modified the catalyst by adding various lanthanide metals at different loading levels. Lanthanide metals investigated in this study were Ce, Gd, La, and Yb. Between two types of synthesis methods, wet-impregnation and modified sol–gel, catalysts synthesized by the latter method provided higher surface areas by 2–10-fold compared to wet-impregnated catalysts (Table 1). A set of standard reaction conditions ($NO = 1780$ ppm, $CH_4 = 2.13\%$, $O_2 = 4\%$ in balance He, 500°C, 61 cm^3(STP)/min) was applied to each catalyst to test its NO reduction activity in the presence of oxygen. Fig. 1 illustrates the results of NO conversion in $NO + CH_4 + O_2$ reaction at 500°C over four different catalysts with varying O_2 concentration. As we reported previously, 100% NO conversion was obtained up to 8800 ppm O_2 concentration over

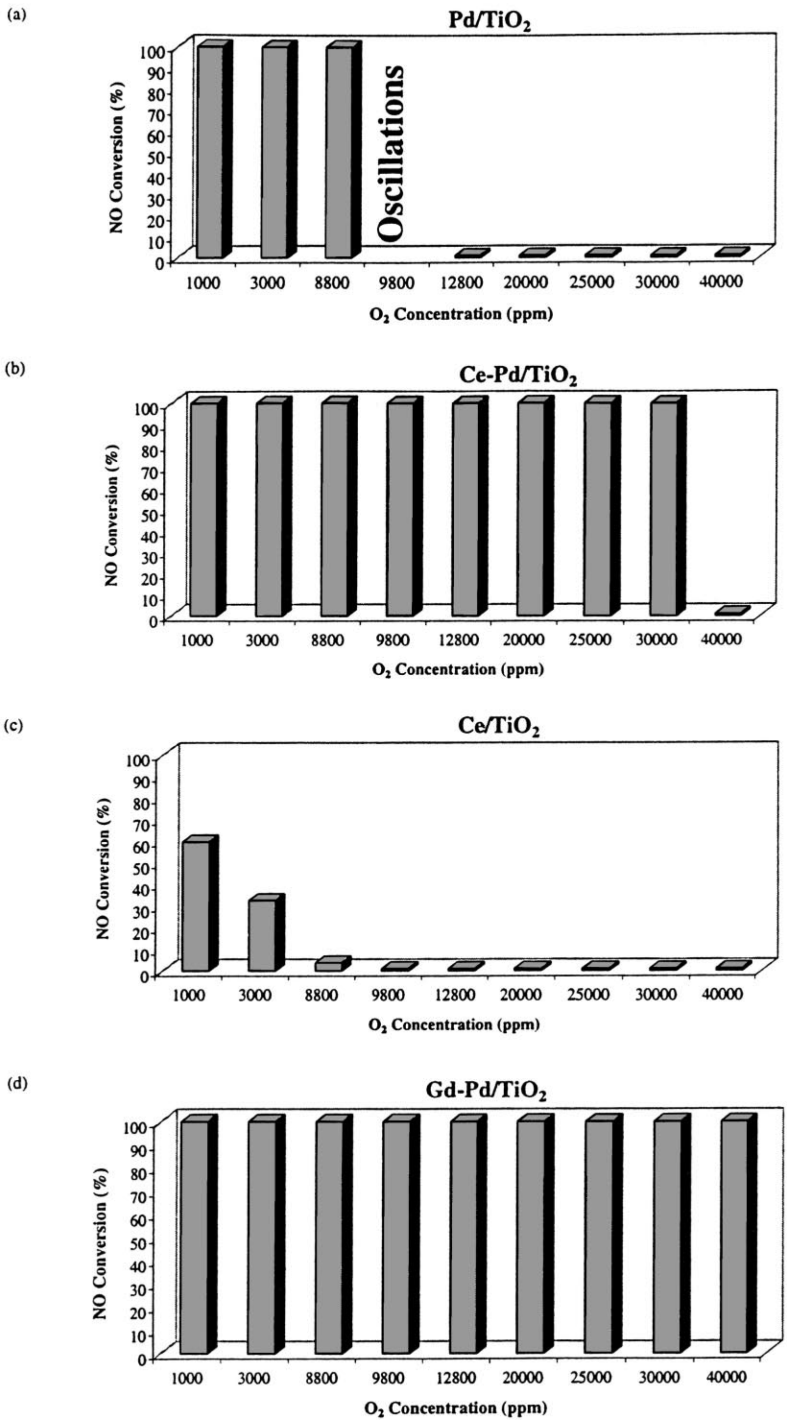

Fig. 1. NO conversion vs. O_2 concentration (1780 ppm NO, 2.13% CH_4, 500°C, 61 cm^3(STP)/min). (a) Pd/TiO_2, (b) Ce–Pd/TiO_2, (c) Ce/TiO_2, (d) Gd–Pd/TiO_2.

Table 1
Specific surface areas (m^2/g) of different catalyst formulations

Catalysts	Preparation	Specific surface area (m^2/g)
2% Pd/TiO_2	wet impregnation	19
1% $Ce/2\%Pd/TiO_2$	wet impregnation	12
2% Pd/TiO_2	sol–gel	80
0.5% Ce/2% Pd/TiO_2	sol–gel	76
1% Ce/2% Pd/TiO_2	sol–gel	28
2% Ce/2% Pd/TiO_2	sol–gel	94
0.5% Gd/2% Pd/TiO_2	sol–gel	123
1% Ge/2% Pd/TiO_2	sol–gel	79
1% Gd/1% Ce/2% Pd/TiO_2	sol–gel	85
1% La/2% Pd/TiO_2	sol–gel	82
1% Yb/2% Pd/TiO_2	sol–gel	66

Pd/TiO_2 and the oscillation behavior was observed at 9800 ppm followed by deactivation of the catalyst. With the wet-impregnated Ce–Pd catalyst, the highest O_2 concentration achieved while giving a 100% NO conversion was 30,000 ppm (Fig. 1(b)). When a catalyst was prepared without Pd (1% Ce/TiO_2), it did not work effectively for the reduction of NO (Fig. 1(c)). The maximum NO conversion was 62% even with 1000 ppm O_2 in feed and it continuously decreased with an increase in O_2 concentration. The La-, Yb-, Ce-, Gd-doped catalysts synthesized by a modified sol–gel method as well as the Pd-only catalyst, which was prepared by the same method all showed higher oxygen resistance than the wet-impregnated catalysts. However, with addition of Gd, the highest O_2 tolerance was achieved while giving a 100% NO conversion (Fig. 1(d)). No self-induced oscillations were observed in $NO–CH_4–O_2$ reaction over Pd/TiO_2 catalysts doped with lanthanide metals. As oxygen concentration was increased, methane conversion also increased; however, methane was never totally exhausted in any of the experiments.

In a different set of experiments, we performed a comparison of Pd and Pd/Gd catalysts which were prepared by the modified sol–gel method, using an above-stoichiometric oxygen concentration. The concentrations of NO, CH_4, and O_2 were 500 ppm, 1.065%, and 2.15%, respectively. We were successfully able to reduce NO with 99.8% conversion with 96.4% selectivity to nitrogen, defined as (2 × moles of N_2 formed/moles of NO converted) while Pd-only catalyst only gave a 4.7% conversion of NO.

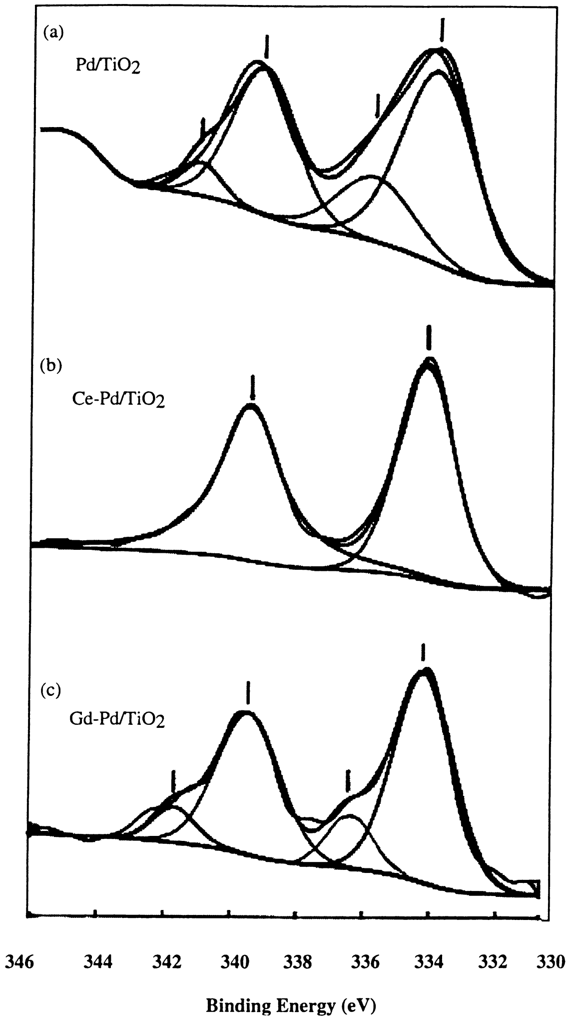

Fig. 2. Pd 3*d* controlled-atmosphere XPS spectra of reduced catalysts prepared in 33% H_2 in He at 200°C for 30 min. (a) Pd/TiO_2, (b) $Ce–Pd/TiO_2$, (c) $Gd–Pd/TiO_2$.

We narrowed our focus on surface characterization to the most promising SCR catalysts, namely Ce- and Gd-doped catalysts. Fig. 2 presents the Pd 3*d* X-ray photoelectron spectra of reduced Pd/TiO_2, $Ce–Pd/TiO_2$, and $Gd–Pd/TiO_2$ catalysts. The reduction of catalysts was performed in a mixture of 33% H_2 in He for 30 min at 200°C and transferred to the XPS chamber without exposing them to the atmosphere. The Pd $3d_{5/2}$ and Pd $3d_{3/2}$ peaks at zero oxidation state are present at 334.1 and 339.5 eV, respectively. The completely oxidized catalyst gave Pd

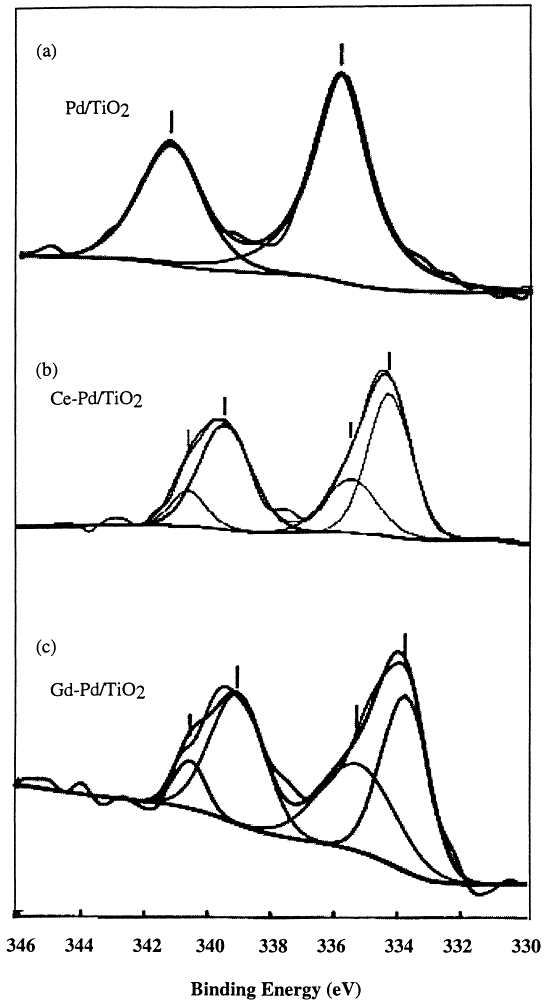

Fig. 3. Pd 3*d* controlled-atmosphere XPS spectra of post-reaction catalysts. (a) Pd/TiO$_2$ exposed to a mixture of 1780 ppm NO, 2.13% CH$_4$, 30,000 ppm O$_2$ at 500°C; (b) Ce–Pd/TiO$_2$ exposed to a mixture of 1780 ppm NO, 2.13% CH$_4$, 30,000 ppm O$_2$ at 500°C; (c) Gd–Pd/TiO$_2$ exposed to a mixture of 1780 ppm NO, 2.13% CH$_4$, 40,000 ppm O$_2$ at 500°C.

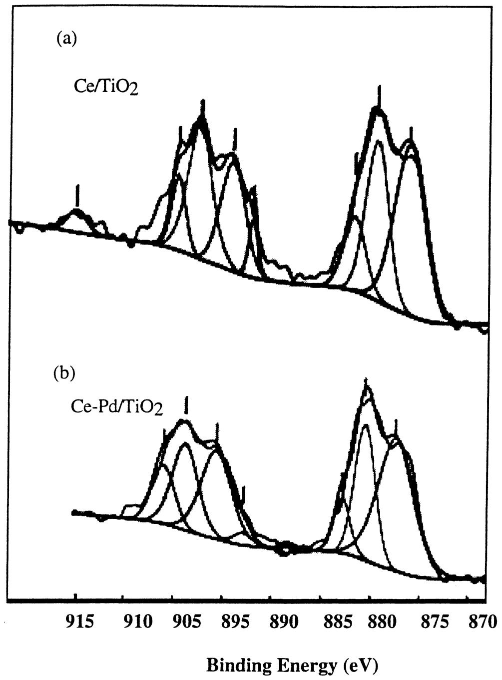

Fig. 4. Ce 3*d* controlled-atmosphere XPS spectra of reduced catalysts prepared in 33% H$_2$ in He at 200°C for 30 min. (a) Ce/TiO$_2$, (b) Ce–Pd/TiO$_2$.

3$d_{5/2}$ and Pd 3$d_{3/2}$ peaks at 335.3 and 340.5 eV, respectively. On the reduced Pd/TiO$_2$ catalyst, Pd was found to exist in both oxide and metallic phases. Deconvolution of these peaks showed that 79% of palladium was in zero state and 21% was in +2 state (Fig. 2(a)). Interestingly, when Ce (1 wt%) was added to the Pd/TiO$_2$ catalyst, 100% of surface palladium was found in metallic phase after it was treated under the same conditions (Fig. 2(b)). When the lanthanide dopant was changed from Ce to Gd, it showed a change in reducibility of palladium. Fig. 2(c) shows that 1% Gd/2% Pd/TiO$_2$ catalyst maintains 84% of the Pd sites in the metallic phase; however, 16% remained in the oxide phase.

The post-reaction X-ray photoelectron spectra of the same set of catalysts are presented in Fig. 3. The spectrum was taken after our standard reaction conditions were applied to each catalyst and transferred to the XPS chamber without exposing them to the atmosphere. Pd only and Ce–Pd catalysts were subjected to O$_2$ concentration of 30,000 ppm that resulted in immediate deactivation of the former catalyst while the latter sample remained active giving a 100% NO conversion. The O$_2$ concentration for Gd–Pd catalyst was 40,000 ppm which also gave a 100% NO conversion. Fig. 3(a) shows the complete oxidation of Pd in the deactivated Pd/TiO$_2$ catalyst. The post-reaction Pd 3*d* XPS spectrum of Ce–Pd catalyst under the same condition showed that 74% of palladium still remained in metallic phase (Fig. 3(b)). The post-reaction characterization of the Gd–Pd catalyst also showed that

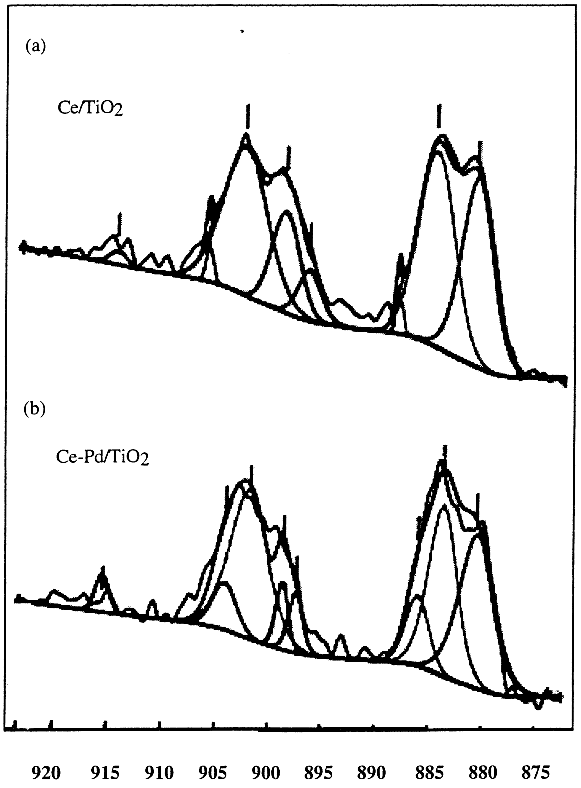

Fig. 5. Ce 3*d* controlled-atmosphere XPS spectra of post-reaction catalysts. (a) Ce/TiO_2 exposed to a mixture of 1780 ppm NO, 2.13% CH_4, 30,000 ppm O_2 at 500°C; (b) Ce–Pd/TiO_2 exposed to a mixture of 1780 ppm NO, 2.13% CH_4, 30,000 ppm O_2 at 500°C.

more than 66% of the Pd sites on the surface was in the zero oxidation state.

Further, Ce 3*d* X-ray photoelectron spectra of reduced and post-reacted 1% Ce/TiO_2 and 1% Ce/2% Pd/TiO_2 catalysts were compared to gain a better understanding of the role of Ce in the chemical state of palladium. Shyu and Otto have investigated Pt/γ–alumina system containing ceria and correlated the amount of CeO_2 present to the %u‴ in Ce 3*d* region where u‴ (915.6 eV) represents the satellite peak which appears only with the presence of Ce^{+4} [14,15]. They reported the correlation between %u‴ and %CeO_2 to be linear. In the reduced XPS spectra, the Ce only catalyst showed a small peak at 915.6 eV whereas Ce–Pd catalyst showed no peak at that binding energy value (Fig. 4). In the post-reaction XPS spectra of Ce only and Ce–Pd catalysts, %u‴ were obtained to be 1% and 2%, respectively (Fig. 5). Pure CeO_2 should have a u‴ area percentage of ≈13% according to Shyu and Otto. Since both of our post-reaction samples contained a u‴ peak percentage much lower than 13%, we can safely conclude that a mixture of +3 and +4 was present after the catalyst was subjected to the reaction conditions. The fact that there was no CeO_2 present on the reduced Ce–Pd catalyst indicates that the presence of palladium helps Ceria be in the +3 chemical state. Ceria is considered in the literature as an oxygen scavenging material which can adjust the surface oxygen concentration during a reaction. The loading of cerium was very small (1 wt%); however, it was enough to keep the palladium from complete oxidation to PdO in the presence of 3% O_2 concentration.

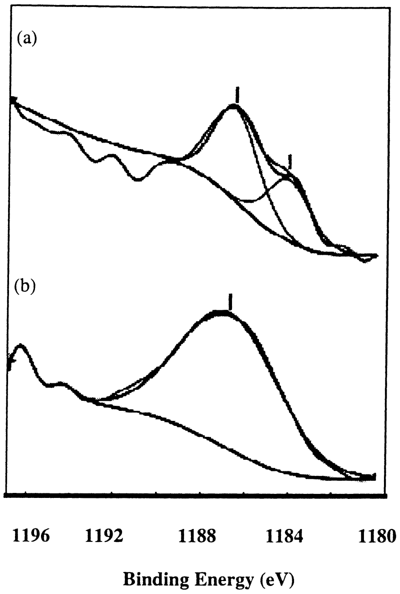

Fig. 6. Gd $3d_{5/2}$ controlled-atmosphere XPS spectra of Gd–Pd/TiO_2 catalyst. (a) Gd–Pd/TiO_2 reduced in 33% H_2 in He at 200°C for 30 min; (b) Gd–Pd/TiO_2 calcined in 100% O_2 at 500°C for 4 h.

The Gd $3d_{5/2}$ XP spectrum of reduced Gd–Pd catalyst is illustrated in Fig. 6. The binding energy value in the +3 state of Gd is 1187.5 eV. The satellite feature exhibited as shoulder can be due to the charge transfer processes from O (2*P*) to Gd (4*f*) [22,23]. After the reduction of the Gd–Pd catalyst, Gd was observed to be present only in the +3 state as observed in the

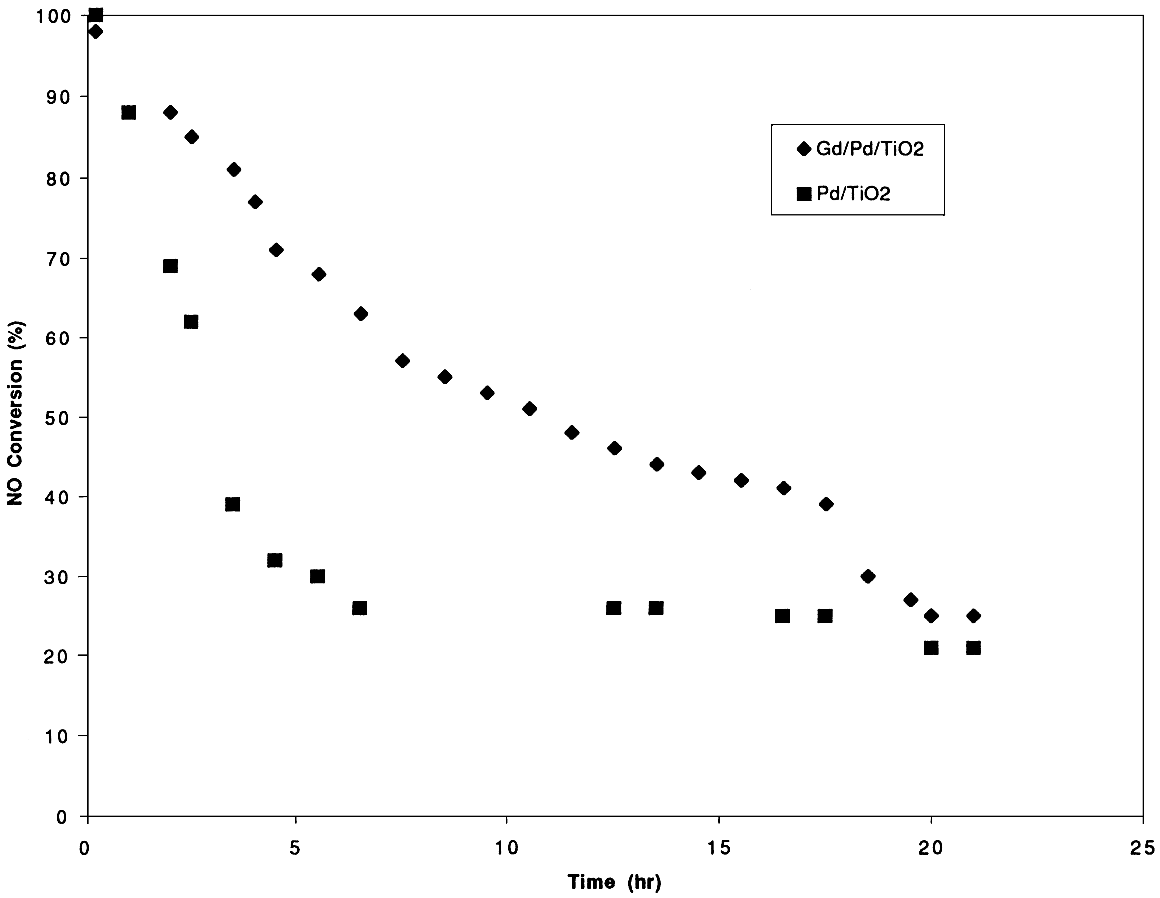

Fig. 7. NO conversion vs. SO_2 time on stream for Pd/TiO_2 and $Gd–Pd/TiO_2$ catalysts (500 ppm NO, 1.065% CH_4 at 500°C, 45 cm^3(STP)/min).

case of Ce (Fig. 6(a)). Over the post-reaction sample, we could not obtain a good signal possibly due to low concentration of Gd on surface. However, the Gd–Pd sample which was treated in oxygen at 500°C for 4 h showed a single peak at 1186.7 eV on the Gd $3d_{5/2}$ XPS spectrum (Fig. 6(b)). The peak position of Gd $3d_{5/2}$ was in agreement with value reported by Christopher et al. [23]. This led us to suggest that under the reaction conditions, Gd would still be still in +3 chemical state.

3.2. *Effect of SO_2*

The effect of SO_2 on the NO reduction with CH_4 over supported Pd and Gd–Pd catalysts synthesized by a modified sol–gel method was investigated by performing steady-state reaction experiments. The feed concentrations used for NO, CH_4, O_2, and SO_2 were 500 ppm, 1.065%, 2%, and 145 ppm, respectively. The flow rate and the temperature used were 45 cm^3(STP)/min and 500°C, respectively. After obtaining a steady-state and near complete NO conversion with the $NO + CH_4 + O_2$ feed mixture, SO_2 was added to observe its effect on the catalytic activity. Immediately after the injection of SO_2, the NO conversion started dropping slowly but steadily. Over the Gd–Pd catalyst, more than 70% conversion was obtained for over 6 h after SO_2 was added to the feed mixture. Over the Pd only catalyst, a sharper drop was observed. After ca. 17 h on stream, the NO conversion reached the steady-state around 25%. Fig. 7 shows the variation of NO conversion with time at 0 and 145 ppm of SO_2 concentration values during

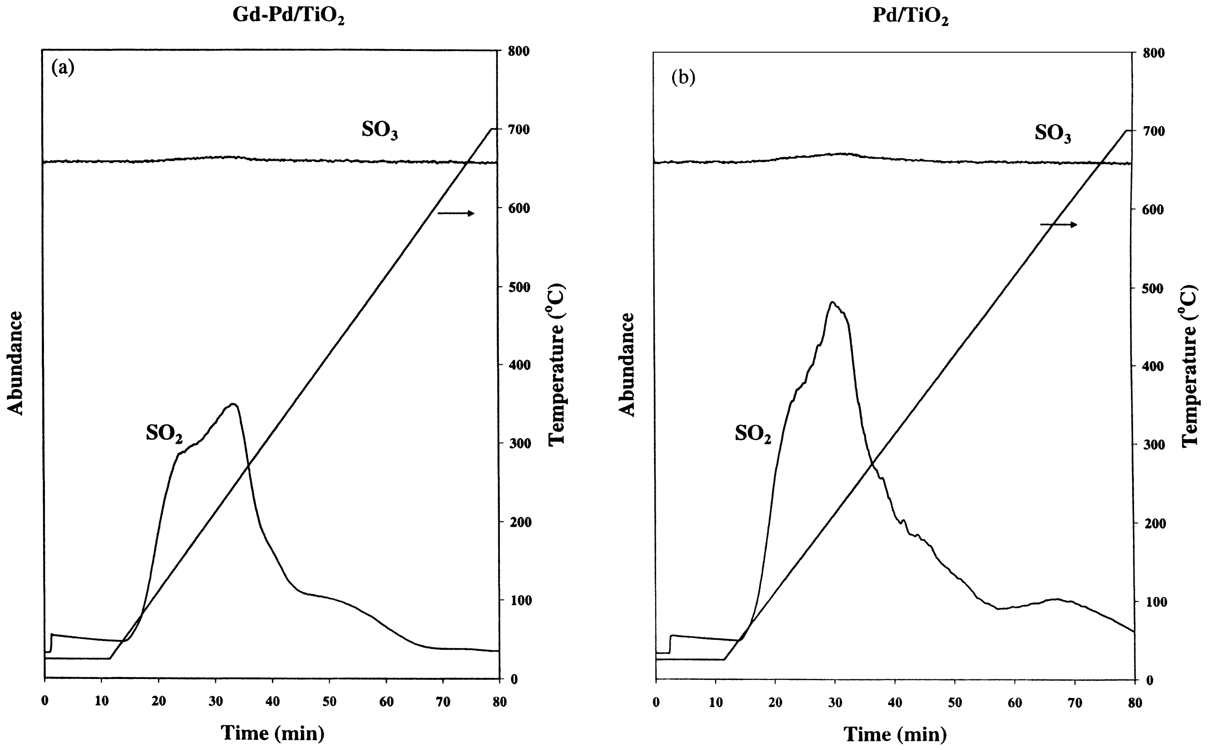

Fig. 8. SO_2 temperature program desorption profiles over reduced catalysts prepared in 33% H_2 in He at 200°C for 2 h. (a) Gd–Pd/TiO_2, (b) Pd/TiO_2.

the first 22 h on stream. The NO conversion on both catalysts dropped significantly; however, the resistance to SO_2 was improved moderately by employing different catalyst synthesis technique and adding Gd. We have reported the effect of SO_2 over Pd/TiO_2 prepared by wet-impregnation to have an immediate and irreversible poisoning effect [21]. Over, the supported Gd–Pd catalyst, the reversibility of the effect of SO_2 was examined by removing the SO_2 feed after 19 h of SO_2 on stream. The NO conversion increased slightly; however, it did not return to the pre-SO_2 level.

The post-reaction S 2*p* XPS spectrum of the same catalyst shows a single peak at 168.3 eV which confirms the existence of sulfur on the surface most likely as a sulfate rather than a sulfide. Further validation of sulfate formation could not be obtained from the formation of small shoulder in the O 1*s* XPS spectrum as we reported previously due to dilute SO_2 concentration used in this study. In order to corroborate the formation of sulfate on the catalyst surface with the presence of SO_2, TPD experiments were performed using a mixture of 1 mol% SO_2 in He. The SO_2 TPD profiles of reduced Gd–Pd/TiO_2 and Pd/TiO_2 are presented in Fig. 8. The SO_2 desorption profiles are similar between the two catalysts mainly consisting of two sharp desorption peaks at 150° and 250°C and a broad peak positioning between 350° and 580°C for Gd–Pd/TiO_2 and one shifted to a higher temperature range by ≈100°C for Pd/TiO_2. A small amount of SO_3 desorption was also observed indicating that the formation of sulfate was possible.

3.3. *Effect of H_2O*

Another stack gas constituent that would be concerned in the reduction of NO over SCR catalysts is H_2O. We investigated the effect of H_2O over the Gd–Pd/TiO2 catalyst in the concentration range between 0% and 6.6% in the steady-state reaction experiment. As we performed in the SO_2 experiments, we waited until the steady-state and a near complete NO conversion were established before the introduction of H_2O. The catalyst was on-line for over 18 h with the addition of water while the NO conversion remained over 99.5%. The nitrogen and carbon-containing species observed in the product stream were N_2, NH_3 and CO_2 that were consistent with those obtained without H_2O. The N_2 selectivity remained around 96.5% even after the injection of 6.6% water. While the steam reforming reaction between methane and water taking place producing CO and H_2 remains a possibility, there was no CO detected. If produced, the concentration of CO would have been smaller than 100 ppm which is under the GC detection limit. The presence of H_2 can increase the NH_3 production which, in turn, lower the N_2 selectivity. However, there was not much change in N_2 selectivity, either.

4. Conclusions

- The addition of Gd–Pd/TiO_2 catalyst increased the oxygen tolerance significantly while giving a 100% NO conversion and eliminated the self-induced oscillation behavior.
- XPS results indicate that the presence of Gd and Ce helps palladium under the reaction conditions to be mainly in metallic phase.
- Over the Gd–Pd catalyst, more than 70% NO conversion was obtained for over 6 h after SO_2 (145 ppm) was added to the feed mixture while a sharper drop in NO conversion was observed over Pd only catalyst.
- The presence of H_2O (0–6.6%) in the feed mixture did not deactivate the catalyst giving a 99.5% NO conversion and 96.5% N_2 selectivity over Gd–Pd catalyst.

Acknowledgements

Financial support provided for this work by the National Science Foundation through Grant CTS-9412544 and from Ohio Coal Development Office is gratefully acknowledged.

References

[1] J.N. Armor, Catal. Today 26 (1995b) 147.
[2] Y. Nishizaka, M. Misono, Chem. Lett. (1993) 1295.
[3] B.K. Cho, B.H. Shanks, J.E. Bailey, J. Catal. 115 (1989) 486.
[4] S.H. Oh, J. Catal. 124 (1990) 477.
[5] G.S. Zafiris, R.J. Gorte, J. Catal. 139 (1993) 561.
[6] J.M. Schwartz, L.D. Schmidt, J. Catal. 148 (1994) 22.
[7] G.S. Zafiris, R.J. Gorte, Surf. Sci. 276 (1992) 86.
[8] J.R. Gonzalez-Velasco, J. Entrena, J.A. Gonzalez-Marcos, J.I. Gutierrez-Ortiz, M.A. Gutierrez-Ortiz, Appl. Catal. B: Environmental 3 (1994) 191.
[9] P. Marecot, A. Fakche, L. Pirault, C. Geron, G. Mabilon, M. Prigent, J. Barbier, Appl. Catal. B: Environmental 5 (1994) 43.
[10] H. Muraki, K. Yokota, Y. Fujitani, Appl. Catal. 48 (1989) 93.
[11] Z. Hu, C.Z. Wan, Y.K. Lui, J. Dettling, J.J. Steger, Catal. Today. 30 (1996) 83.
[12] Y. Zhang, M. Flytzani-Stephanopolous, J. Catal. 164 (1996) 131.
[13] D.A. Kay, W.G. Wilson, V. Jalan, J. Alloys and Compounds 192 (1993) 11.
[14] J.Z. Shyu, K. Otto, W.L.H. Watkins, G.W. Graham, R.K. Belitz, H.S. Gandhi, J. Catal. 114 (1988) 23.
[15] J.Z. Shyu, K. Otto, J. Catal. 115 (1989) 16.
[16] B.K. Cho, J. Catal. 131 (1991) 74.
[17] B. Dziewiecka, Z. Dziewiecki, Catal. Today 17 (1993) 121.
[18] M.W. Kumthekar, U.S. Ozkan, J. Catal. 171 (1997) 45.
[19] M.W. Kumthekar, U.S. Ozkan, J. Catal. 171 (1997) 54.
[20] U.S. Ozkan, M.W. Kumthekar, G. Karakas, J. Catal. 171 (1997) 67.
[21] J. Mitome, G. Karakas, K. Ryan, U.S. Ozkan, Appl. Catal. B: Environmental 42 (1998) 3.
[22] P. Burroughs, A. Hamnett, A.F. Orchard, G. Thornton, J. Chem. Soc. Dalton Trans. 17 (1976) 1686.
[23] J. Christopher, C.S. Swamy, J. Material Science 26 (1991) 4966.