

Catalytic reduction of N₂O and NO₂ with methane over sol–gel palladium-based catalysts

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Abstract

Pd/TiO₂ and Gd-doped Pd/TiO₂ prepared through a ‘one-pot’ sol–gel method are shown to be active for the reduction of both N₂O and NO₂ using CH₄ as a reducing agent under excess O₂ conditions. In previous studies these catalysts were shown to effectively reduce NO with CH₄, however activity was strongly dependant on the oxidation state of Pd. Through the electropositive nature of Gd, Pd was maintained in metallic state under higher oxygen concentrations compared to the Gd-free catalysts. Characterization through XPS and in situ DRIFTS studies indicate that in the reduction of NO₂, even under excess oxygen, a significant portion of the surface Pd is maintained in the active metallic state. © 2006 Elsevier B.V. All rights reserved.

Keywords: N₂O; NO₂ reduction; Palladium; Gadolinium; Methane

1. Introduction

As a significant source of pollution from combustion sources, nitrogen oxides (NO_x) have been the focus of much regulatory and research attention. Various NO_x species are known to contribute to the greenhouse effect, acid rain formation, and to play a key role in initiating the formation of ground level smog and ozone. The best current NO_x control technology for stationary sources is selective catalytic reduction (SCR) with NH₃. Problems associated with the current SCR technology, particularly the storage and safety issues associated with NH₃ use, have raised interest in the development of catalysts capable of using alternative reducing agents. Methane is an especially attractive candidate because of its relative high abundance and low cost. The principle challenges to methane use are difficulty in activating it, and selectively using it as a NO_x reduction agent in oxygen rich streams.

Since the early 1990s many different catalyst formulations have been investigated for the catalytic reduction of NO with methane in the presence of oxygen, including metal exchanged zeolitic catalysts such as Co/ZSM-5 [1–3], Pd–H–ZSM-5 and

Pd–Ce–H–ZSM-5 [4–6]. Vannice and co-workers [7,8] have studied a group of non-zeolitic catalysts based on La₂O₃, CeO₂, Nd₂O₃, Sn₂O₃, Tm₂O₃, and Lu₂O₃. Nobel metals such as Pd, Pt, and Rh supported on silica and/or alumina were also investigated for NO–CH₄ reaction with and without the presence of oxygen [9–10]. A few researchers have investigated the use of titania supported palladium catalysts for the reduction of NO. Ueda et al. [11] studied the reduction of NO using hydrogen in the presence of oxygen and water vapor.

We have previously reported the effective use of Pd-based catalysts supported on titania for the NO reduction with CH₄ in the presence of O₂ [12–22]. The extent of the reaction was shown to be highly dependent on the palladium oxidation state, with the metallic phase of palladium necessary for the reduction of NO to N₂. We extensively studied the mechanistic aspects of NO/CH₄ reactions using isotopic labeling techniques under both steady-state and transient conditions. From a series of unsteady-state and steady-state isotopic labeling studies using labeled species such as ¹⁵N¹⁶O, ¹⁵N¹⁸O, ¹³CH₄, ¹⁸O₂, it was concluded that N₂ is formed through direct participation of CH₄, possibly through a methyl–nitrosyl type intermediate, whereas N₂O formation was mainly a result of the NO decomposition reaction [13]. We also used steady-state oscillations as a probe to gain insight into the reaction network and found that the oxidation state of the active metal was responsible for three competing reactions; NO reduction with CH₄, direct CH₄ oxidation, and NO decomposi-

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tion [14]. In situ DRIFTS was used to identify adsorbed species under NO, NO + CH₄, and NO + CH₄ + O₂ flow, and the formation of various nitrogen-oxo adspecies such as bridged/bidentate nitrate, monodentate nitrate, nitro, and linear NO was confirmed. It was found that linearly adsorbed NO species on Pd, with a IR absorption band at 1780 cm⁻¹, was dominant on reduced Gd–Pd/TiO₂ at high temperatures under NO flow. However, the intensity of nitrate species was increased on an oxidized surface relative to the linear NO. Based on these results, the key surface species under reaction conditions were determined to be CH_x, NH_x, monodentate nitrate, nitro, and linear NO species [20–22].

Other groups have also shown in situ FTIR to be a powerful technique in the elucidation of reaction mechanisms [23–26]. Over Co-FER, Li and Armor [24] used DRIFTS techniques to propose a possible mechanism for the NO–CH₄–O₂ reaction. According to their proposed mechanism, formation of bound NO₂ on Co²⁺ sites is the first step, which is followed by CH₄ activation by the bound NO₂, forming CH₃• radicals. The CH₃• radical could react with bound NO₂ to form nitromethane (CH₃NO₂), which further reacts with gas phase NO to N₂, H₂O, and CO₂ (23). Lobree et al. observed Co²⁺–CN and Al³⁺–NCO species during the NO reduction with CH₄. The reaction rate of CN species was determined to be faster with NO₂ than with O₂ and NO. Possible mechanistic steps include the formation of surface nitrosomethane (CH₃NO). Over Mn–ZSM-5 catalyst, Mn²⁺ is slowly oxidized to Mn³⁺ by NO adsorption and simultaneously, Mn²⁺(NO) and Mn³⁺(O⁻)(NO) species are formed. Again, CN species were formed and shown to react rapidly with NO₂ (25). Other researchers propose that methyl species combine directly with adsorbed NO₂ to form nitromethane (CH₃NO₂). A mechanistic study of NO–CH₄–O₂ reaction over Co–ZSM-5 was also conducted by Sun et al. [26] using DRIFTS. The presence of O₂ enhanced NO oxidation to form adsorbed NO₂. The authors suggested that the adsorbed NO₂ could react with methane to generate nitromethane intermediates.

Here we focus on the activity of Pd/TiO₂ and Gd–Pd/TiO₂ catalysts toward the reduction of N₂O and NO₂ with CH₄ in the presence of O₂. Additionally, characterization of the adsorption properties of these catalysts studied through TPD and in situ DRIFTS is presented.

2. Experimental

2.1. Catalyst preparation

The catalysts examined in this study were 2%Pd/TiO₂ and 1%Gd/2%Pd/TiO₂, prepared by a modified ‘one-pot’ sol–gel method. The precursors utilized were palladium acetate, titanium(IV) isopropoxide, and gadolinium nitrate, all obtained from Aldrich.

In both catalyst preparations, palladium acetate was dissolved in isopropyl alcohol and titanium(IV) isopropoxide was added to the palladium solution under continuous stirring at room temperature. For the bimetallic catalyst a solution of gadolinium nitrate in water was added drop-wise with a syringe pump to this suspension. For the Pd-only catalyst, distilled water was

used instead of the Gd solution. After hydrolysis the resulting gel was dried overnight and then calcined at 500 °C for 4 h in air.

2.2. Catalyst characterization

Surface characterization techniques used in this study included X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).

The controlled-atmosphere X-ray photoelectron spectra of post reaction samples were obtained by an ESCALAB MKII ESCA/Auger spectrometer, with a Mg Kα (*hν* = 1253.6 eV) source operated at 15 kV and 20 mA. The charge shift was corrected based upon the standard binding energy of C 1s (284.5 eV).

Temperature programmed desorption (TPD) experiments were conducted using a laboratory-made TPR/TPD system. Desorbing species were detected by an HP5890GC-MS. 75 mg of sample was loaded into a U-shaped quartz reactor and calcined in-situ with 10% oxygen in balance helium at 500 °C for 30 min, followed by flushing in helium for 30 min. Samples were then reduced under 33% hydrogen in balance helium at 200 °C for 30 min, followed again by flushing for 30 min in helium. The sample was then cooled to room temperature under helium flow. Adsorption was performed at room temperature for 1 h followed by helium flushing for 1 h to remove physically adsorbed gas.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were performed using a Bruker IFS66 equipped with a DTGS detector and a KBr beamsplitter. Catalysts were placed in a heated sample cup inside a Spectratech diffuse reflectance cell equipped with KBr windows. An internal thermocouple mount allowed for the direct measurement of the catalyst surface temperature. Each catalyst was pre-treated in situ either by calcination under 10% oxygen at 400 °C or by reduction under 30% hydrogen in balance helium at 200 °C for 30 min, followed by cooling under He. For sequential adsorption studies performed at 300 °C, background spectra were taken at 300 °C under helium before gas species were introduced. For adsorption spectra obtained at several different temperature levels, background spectra were taken under helium at each investigated temperature prior to the introduction of gas species. Each spectrum was averaged over 1000 scans in the mid-IR range (400–4000 cm⁻¹) to a nominal 2 cm⁻¹ resolution.

2.3. Reaction studies

A 1/4 in OD stainless steel reactor was used to perform steady state reaction experiments. All gas lines were heated to 130 °C to prevent water condensation in the system. In all experiments, a catalyst sample of 69 mg was placed inside the reactor and held in place by quartz wool packing. Reaction temperatures were varied from 300 to 500 °C, under control of a PID temperature controller (Omega).

Prior to each run the catalyst bed was reduced under 33% H₂ in He at 200 °C for 30 min. Reaction feed concentrations were 1.065% methane, 500 ppm NO₂ or N₂O, and O₂ to reach

Table 1
Steady state reaction results for the reduction of N₂O with CH₄ over 1%Gd/2%Pd/TiO₂ and 2%Pd/TiO₂

Catalyst	O ₂ /CH ₄ = 1.88			O ₂ /CH ₄ = 2.35		
	N ₂ O conversion (%)	N ₂ selectivity (%)	CH ₄ conversion (%)	N ₂ O conversion (%)	N ₂ selectivity (%)	CH ₄ conversion (%)
1%Gd/2%Pd/TiO ₂	100	100	94	55	100	95
2%Pd/TiO ₂	100	98	84	7	97	93

The reaction was performed under O₂ deficient and excess conditions at 500 °C.

an O₂/CH₄ ratio of 1.88 or 2.35%. Helium (minimum purity 99.995%) was used as the balance gas. Steady-state was generally reached within 1 h, however typical reaction times were 4 h. Both reactants and reaction products were quantified by a HP 5890A gas chromatograph equipped with a molecular sieve and a pora-pak column operating at 80 °C (nitrous oxide, nitrogen, oxygen, methane, carbon monoxide, and carbon dioxide), by an IR ammonia analyzer (Siemens Ultramat 5F), and by a chemiluminescence NO–NO₂–NO_x analyzer (Thermo Environmental Instruments, Model 42H). Nitrogen and carbon balances were always close to 100%. For this work NO₂ and N₂O conversions were defined as (NO_x consumed)/(NO_x Fed). N₂ selectivity was calculated as (N₂ produced)/(NO_x consumed) for N₂O reactions, and twice this number for NO₂ reactions.

3. Results and discussion

3.1. Reduction of N₂O with CH₄

Reduction of N₂O over Pd/TiO₂ and Gd–Pd/TiO₂ catalysts was examined at O₂/CH₄ concentration ratios of 1.88 and 2.35. The N₂O conversions and N₂ selectivities obtained at 500 °C are presented in Table 1. At the oxygen-deficient conditions, complete N₂O conversion is achieved over both catalysts with N₂ selectivities approaching 100%. The only other N-containing product besides N₂ was NH₃ and was observed only on Pd/TiO₂ catalyst. When the O₂ concentration was increased, there was a decrease in N₂O conversion over both catalysts, but the drop was much more significant over the Pd-only catalyst. CH₄ conversions in these experiments was high and was observed to increase with increasing O₂ concentration.

The N₂O reduction with CH₄ was also investigated at different temperatures and an O₂/CH₄ ratio of 1.88 (Table 2). In these experiments, the only nitrogen containing products observed were nitrogen and ammonia. N₂O conversion increased with temperature in the range of 350–500 °C, and was slightly higher over the bimetallic catalyst at low temperature. By 500 °C, complete N₂O conversion was obtained over both catalysts. Selec-

Table 2
Effect of temperature on the N₂O reduction with CH₄ over 1%Gd/2%Pd/TiO₂ and 2%Pd/TiO₂ catalysts

	350 °C (%)	400 °C (%)	450 °C (%)	500 °C (%)
1%Gd/2%Pd/TiO ₂				
N ₂ O conversion	19	25	68	100
N ₂ selectivity	99	97	99	99
CH ₄ conversion	27	51	92	94
2%Pd/TiO ₂				
N ₂ O conversion	4	10	84	100
N ₂ selectivity	97	98	98	98
CH ₄ conversion	18	38	75	84

tivity was nearly 100% for both catalysts across the temperature range. CH₄ conversion was observed to increase with temperature over both catalysts. At a given reaction temperature the conversion was higher over the bimetallic catalyst, which corresponded to higher N₂ yields.

3.2. Reduction of NO₂ with CH₄

Table 3 shows the reduction of NO₂ with CH₄ at 500 °C over Pd/TiO₂ and Gd–Pd/TiO₂. NO₂ conversion was above 95% for both oxygen deficient and excess conditions. At an O₂/CH₄ ratio of 1.88 N₂ selectivity on the Pd-only catalyst was nearly 100%, but decreased in excess oxygen reaching only 55%. Corresponding to the lowered selectivity, the other nitrogen-containing product was NO. In comparison, the Gd–Pd/TiO₂ catalyst did not suffer from a significant N₂ selectivity drop under excess oxygen, where N₂ selectivity remained above 90%. CH₄ conversion over the Gd/Pd catalyst was above 95% for both O₂ feeds. Over the Pd-only catalyst CH₄ conversion increased with the addition of more O₂.

The effect of temperature on the reduction of NO₂ at an O₂/CH₄ ratio of 1.88 over Gd–Pd and Pd catalysts are shown in Table 4. NO₂ conversion was over 95% at all temperatures between 350 and 500 °C over Gd–Pd, but near 100% N₂ selectivity was achieved only at 500 °C. At the lower temperatures N₂

Table 3
Steady state reaction results for the reduction of NO₂ with CH₄ over 1%Gd/2%Pd/TiO₂ and 2%Pd/TiO₂

Catalyst	O ₂ /CH ₄ = 1.88			O ₂ /CH ₄ = 2.35		
	NO ₂ conversion (%)	N ₂ selectivity (%)	CH ₄ conversion (%)	NO ₂ conversion (%)	N ₂ selectivity (%)	CH ₄ conversion (%)
1%Gd/2%Pd/TiO ₂	100	94	97	100	91	97
2%Pd/TiO ₂	100	98	76	97	54	95

The reaction was performed under O₂ deficient and excess conditions at 500 °C.

Table 4
Effect of temperature on the NO₂ reduction with CH₄ over 1%Gd/2%Pd/TiO₂ and 2%Pd/TiO₂ catalysts

	350 °C (%)	400 °C (%)	450 °C (%)	500 °C (%)
1%Gd/2%Pd/TiO ₂				
NO ₂ conversion	95	96	99	100
N ₂ selectivity	53	51	67	97
CH ₄ conversion	15	30	76	97
2%Pd/TiO ₂				
NO ₂ conversion	90	90	92	97
N ₂ selectivity	50	57	61	54
CH ₄ conversion	20	43	55	76

selectivity was between 50 and 60%, with the other N-containing product being NO. NO₂ conversions over the Pd only catalysts were somewhat lower, but still remained above 90% at all temperatures tested. N₂ selectivities however, were low in the entire temperature range, with the highest N₂ selectivity being around 60%. Over both catalysts CH₄ conversion increased with reaction temperature, with higher conversions reached over the bimetallic catalyst.

In our previous work, we reported the strong dependence of NO–CH₄ reaction on the oxidation state of Pd, where metallic Pd was shown to be necessary for the selective NO reduction with CH₄ while Pd²⁺ led to combustion of the hydrocarbon [17]. Using the oscillatory behavior of the CH₄ + O₂ system over Pd catalysts, we have also shown that Pd can exist in either the metallic or the oxide phase depending on the temperature and oxygen partial pressure (14). At any given oxygen concentration, decreasing the temperature results in the thermodynamic equilibrium shifting toward the oxide phase. In the NO₂ + CH₄ experiments, it is possible that, a larger fraction of Pd exists in the Pd²⁺ state, especially at lower temperatures. This would explain the lower N₂ formation, which is dependent on the metallic Pd sites. The high NO₂ conversions, on the other hand, can be explained by the conversion of NO₂ to NO and O₂ through a decomposition reaction.

Bamwenda and co-workers [45] studied NO₂ decomposition to NO and 1/2O₂ during NO_x reduction with C₃H₆ over Rh, Pt, and Au catalysts supported on alumina. They found that both Rh and Pt were active in converting NO₂ to NO in the presence of oxygen over a temperature range of 200–500 °C, approaching the thermodynamic equilibrium above 400 °C. Since Pd is also a precious metal in the same group as Rh and Pt, it is possible that formation of NO through decomposition of NO₂ took place during NO₂–CH₄–O₂ reaction. Then, NO could be further reduced to N₂ by methane, which is activated on Pd as reported in our previous studies [17]. It is possible that overall NO formation was lower on the Gd-containing catalyst because the rate of reaction for NO reduction with activated methane is faster than the decomposition rate. The fact that only the Gd-containing catalyst is able to reduce NO is consistent with our previous results that this catalyst can maintain Pd in metallic state at higher oxygen concentrations compared to Gd-free catalyst. Direct reduction of NO₂ with CH₄ is also a possibility, however, lower N₂ yields obtained from NO₂ compared to those obtained from NO sug-

gests that, in this case, decomposition of NO₂ may be more prominent than its direct reduction.

3.3. Post-reaction XPS

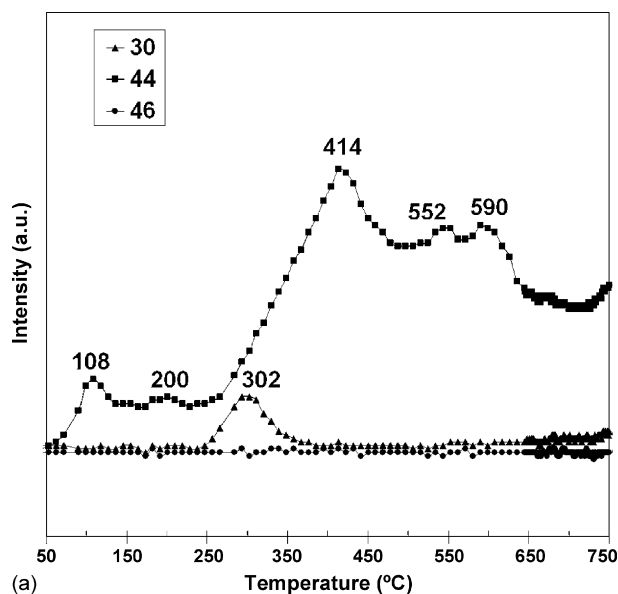
Analysis of the Pd oxidation state over post-reaction catalysts was performed by XPS. After being kept on-stream at 500 °C for 20 h in the NO₂ + CH₄ + O₂ reaction with excess oxygen, the catalyst was transferred from the reactor to the XPS analysis chamber without exposure to the atmosphere. In the XPS results two Pd oxidation states are visible. The zero oxidation state was observed by Pd_{5/2} and Pd_{3/2} peaks at 334.7 and 340.0 eV, respectively. The +2 oxidation state was assigned to peaks at 336.9 and 342.0 eV. Deconvolution of the peaks showed that 40% was present as Pd⁰ and 60% as Pd²⁺. It is important to observe that some Pd was maintained in the reduced state even under excess oxygen reaction conditions, corresponding to the observed reaction activity. For comparison XPS results for the reduced Gd–Pd/TiO₂ showed that 84% of the Pd is present in the metallic phase.

3.4. TPD experiments

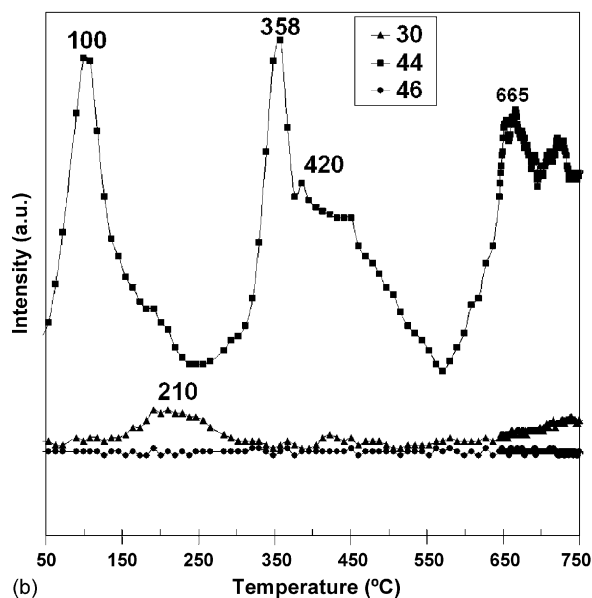
3.4.1. N₂O TPD

Temperature-programmed desorption of N₂O was performed on both reduced and oxidized catalyst samples. Mass to charge ratios of *m/e* = 46 (NO₂), 44 (N₂O), and 30 (NO) are shown. Since *m/e* = 44 corresponds to CO₂ as well as N₂O, *m/e* = 12 corresponding to atomic carbon was also monitored. In all experiments this signal was negligible, indicating that *m/e* = 44 was due only to N₂O desorption. Fig. 1a shows the TPD profiles obtained after adsorption of N₂O over the reduced Gd–Pd bimetallic catalyst. Over this sample, there were N₂O (*m/e* = 44) peaks at 108, 200, and a broad desorption feature with maxima at 414, 552, and 590 °C. We also observed a small NO (*m/e* = 30) desorption peak at around 302 °C, indicating that the catalyst converted N₂O to NO. N₂O TPD from oxidized Gd–Pd sample resulted in desorption features at 100, 180, 358, 420, and 665 °C, as shown in Fig. 1b. The intensity of the low temperature feature is much larger over the oxidized sample. NO desorption was again observed, though the peak temperature was lowered to 210 °C. NO₂ desorption was not observed over either sample.

N₂O desorption profiles from Pd/TiO₂ showed similar behavior to the bimetallic catalysts. Over the reduced Pd/TiO₂ shown in Fig. 2a, desorption features were observed in a broad range with maxima at 384, 458, and 485 °C. In comparison, the oxidized catalyst (Fig. 2b) showed more prominent desorption features at low temperatures, with peaks at 100, 311, 360, and 705 °C. Significant differences in the desorption of NO were observed in comparison to the Gd–Pd samples. Over the reduced sample a large NO desorption peak was observed at 197 °C. This desorption occurs at lower temperature and is of larger intensity than over the reduced bimetallic catalyst. Over the oxidized Pd/TiO₂ shown in Fig. 2b NO desorption was observed at 240 °C, slightly higher temperature than on the bimetallic sample. NO₂ was not observed in either experiment.



(a)

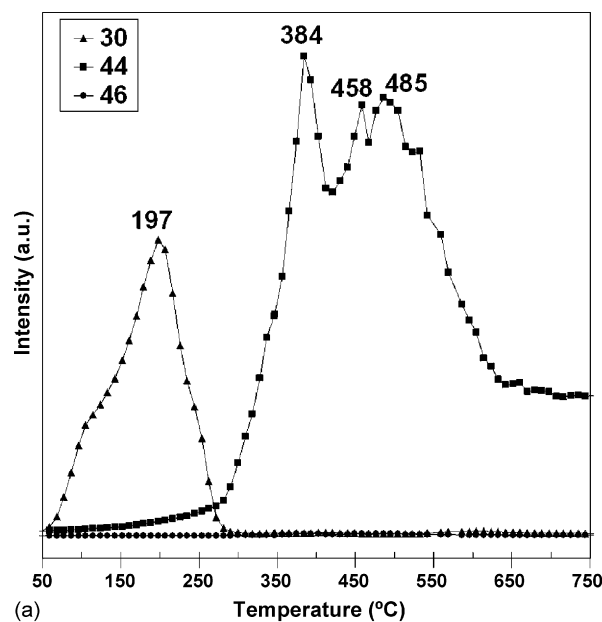


(b)

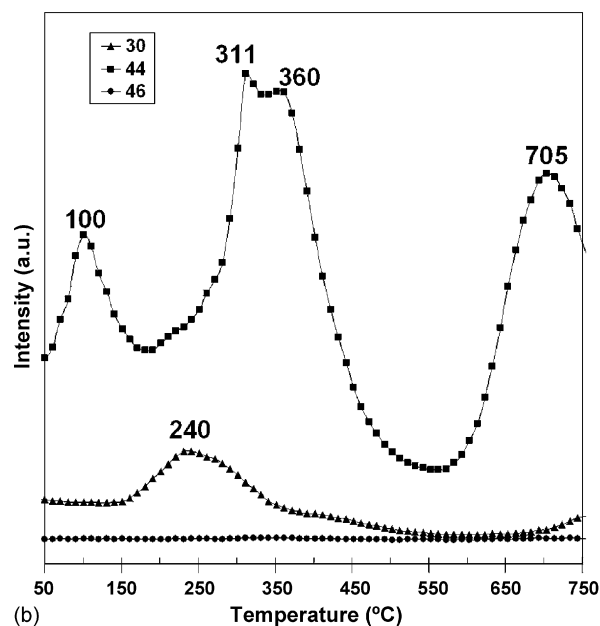
Fig. 1. N_2O TPD profiles of 1%Gd/2%Pd/TiO₂ (a) reduced (b) oxidized. m/e ratios of 30(▲), 44(■), 46(●) correspond to NO, N_2O , NO_2 , respectively.

3.4.2. NO_2 TPD

NO_2 TPD experiments were performed on Gd–Pd and Pd in both the reduced and oxidized states. In examining the results of NO_2 TPD it is important to note that $m/e = 30$ (NO) is the principle ionization fragment of NO_2 . Over the reduced Gd–Pd/TiO₂ catalyst shown in Fig. 3a, NO_2 desorption peaks were observed at 120, 249, and 324 °C. The profile for $m/e = 30$ matches that for $m/e = 46$ closely, indicating that it is due solely to the fragmentation of NO_2 . A small amount of $m/e = 44$ (N_2O) is observed in a broad desorption feature between 200–350 °C. Fig. 3b shows the desorption profiles of the oxidized Gd–Pd sample. Desorption peaks for NO were seen at 117 and 301 °C. The peak at 117 °C was not accompanied by a corresponding $m/e = 46$ peak, suggesting that it is NO desorption. The feature at 301 °C is due to fragmentation of NO_2 as the profiles match closely. The des-



(a)



(b)

Fig. 2. N_2O TPD profiles of 2%Pd/TiO₂ (a) reduced (b) oxidized. m/e ratios of 30(▲), 44(■), 46(●) correspond to NO, N_2O , NO_2 .

orption of N_2O was also observed and coincided with the NO_2 feature at 301 °C. These results indicate that NO_2 decomposition took place over the oxidized catalyst. NO_2 desorption results over reduced and oxidized Pd catalysts in Fig. 4a and b, respectively, were nearly identical to their Gd–Pd counterparts. Peaks were observed in similar locations as well as the same trends in NO_x species production. On the reduced Pd catalyst the two main desorption features were slightly closer in temperature, 149 and 251 °C. Observed NO again seems to be due to NO_2 fragmentation, and only a small amount of N_2O is observed. On the calcined Pd sample a shoulder at 367 °C is observed on the main desorption peak, but otherwise peak shape and location are very similar to the bimetallic sample. This oxidized sample also

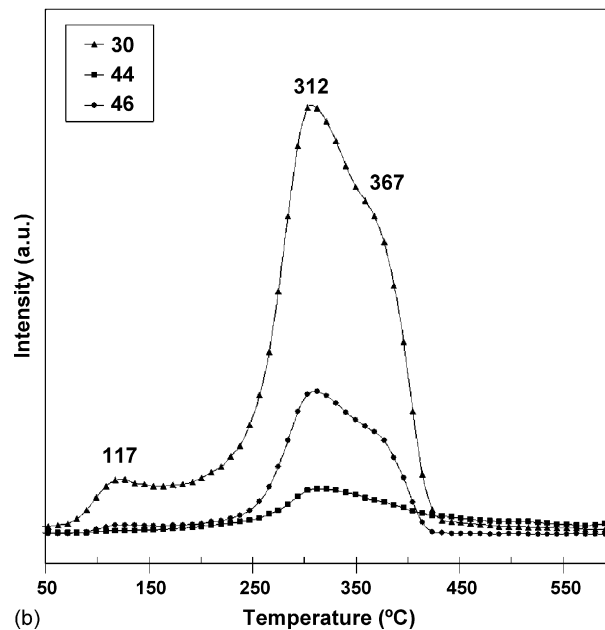
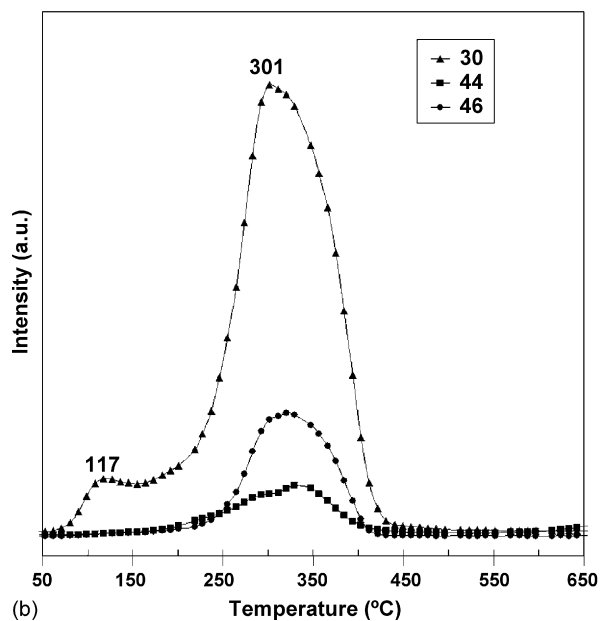
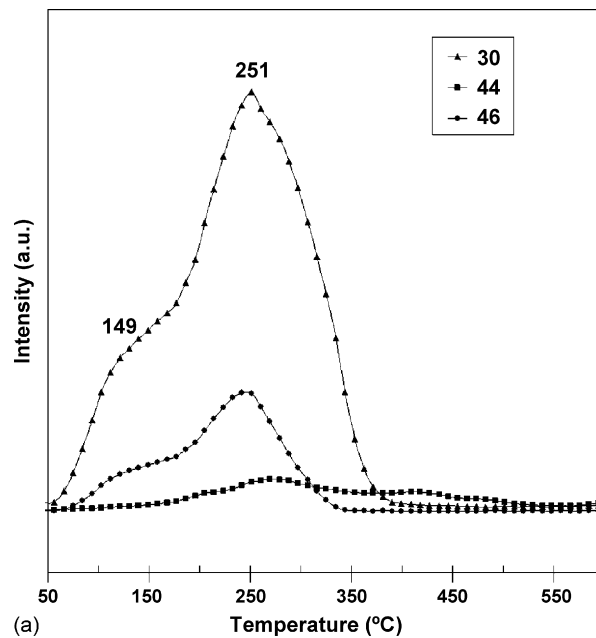
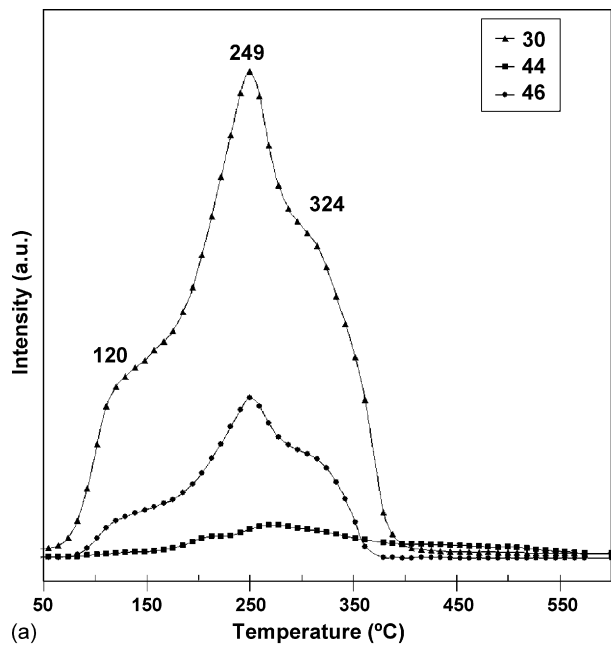


Fig. 3. NO_2 TPD profiles of 1%Gd/2%Pd/TiO₂ (a) reduced (b) oxidized. m/e ratios of 30(▲), 44 (■), 46(●) correspond to NO, N₂O, NO₂.

Fig. 4. NO_2 TPD profiles of 2%Pd/TiO₂ (a) reduced (b) oxidized. m/e ratios of 30 (▲), 44(■), 46(●) correspond to NO, N₂O, NO₂.

appears to be active for NO₂ decomposition as evidenced by NO desorption at 117 °C and N₂O seen near 315 °C. The NO₂ TPD results support our assertion that NO₂ decomposition is more likely to take place over the oxidized catalyst and help explain the trends seen in the reaction experiments.

3.5. DRIFTS experiments

3.5.1. $\text{N}_2\text{O} \rightarrow \text{N}_2\text{O} + \text{CH}_4 \rightarrow \text{N}_2\text{O} + \text{CH}_4 + \text{O}_2 \rightarrow \text{He flush}$

DRIFT spectra were taken over both reduced and oxidized Gd–Pd/TiO₂ catalysts following exposure to feeds of N₂O, N₂O + CH₄, N₂O + CH₄ + O₂ (low O₂ concentration), and N₂O + CH₄ + O₂ (high O₂ concentration), performed in sequence. Gas

concentrations were N₂O = 1780 ppm, CH₄ = 2.13%, O₂ = 0.3 and 4.5%, respectively. Spectra were taken under the gas flows, after the catalysts had been exposed to each gas mixture for 30 min at 300 °C surface temperature.

Fig. 5 shows spectra taken over the reduced Gd–Pd catalyst. Under N₂O flow only, we observed bands at 2200–2240, 2333, 1499, and 1347 cm⁻¹. The doublet at 2200–2240 cm⁻¹ could correspond to gas phase N₂O, but is also indicative of adsorbed N₂O. Wood and co-workers [27] examined N₂O adsorption on zeolitic systems and reported bands in the region 2226–2282 cm⁻¹ associated with N–N stretching, and in 1344–1308 cm⁻¹ due to N–O stretching. They have reported

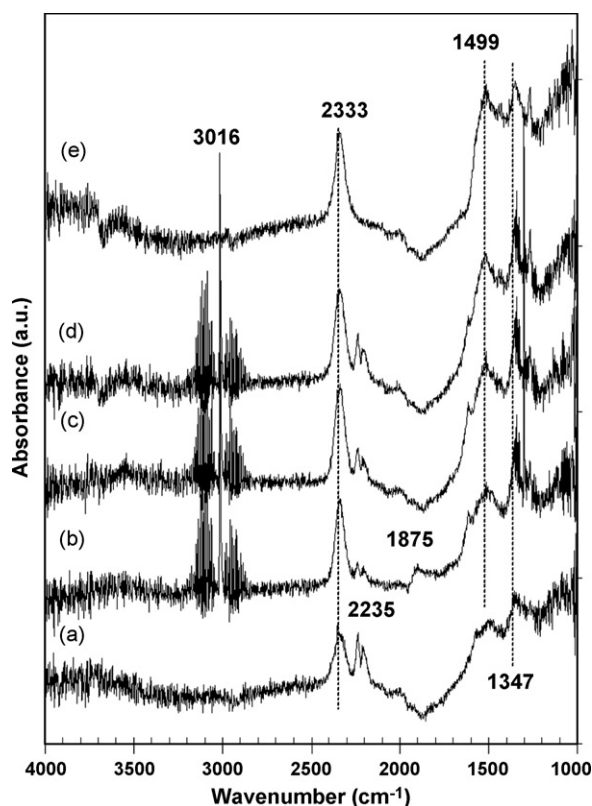


Fig. 5. DRIFT spectra taken during the sequential introduction of reactants at 300 °C to reduced 1%Gd/2%Pd/TiO₂. (a) N₂O, (b) N₂O + CH₄, (c) N₂O + CH₄ + O₂ (low), (d) N₂O + CH₄ + O₂ (excess) and (e) He flush.

that the surface acidity plays a strong role in N₂O adsorption. The band at 2333 cm⁻¹ is in the range reported to be adsorbed dinitrogen [28], which suggests N₂O decomposition to N₂ on the surface. The band at 1499 cm⁻¹ was assigned to NH₄⁺ as [29], likely the result of interaction with Brønsted acid sites on the surface. It is also possible that chemisorbed hydrogen from the reduction step remained on the surface after treatment and interacted with N₂O.

With the introduction of CH₄ to the N₂O flow, gas phase CH₄ is confirmed by the presence of the bands at 3016 and 1306 cm⁻¹. A band at 1875 cm⁻¹ was observed due to the formation of NO, either adsorbed on metal (Pd) cations [30] or in the gas phase. Evidence of the N₂O reduction with CH₄ is observed through several changes in surface species. The intensity of the N₂O doublet at 2199 and 2235 cm⁻¹ decreased upon the addition of CH₄. Simultaneously the band at 2333 cm⁻¹ assigned to adsorbed dinitrogen increases. The formation of H₂O, a product of the reduction reaction, was also observed through a small peak at 1610 cm⁻¹. The doublet in the region of 2350 cm⁻¹ characteristic of CO₂ may not be visible due to the large dinitrogen band.

When 0.3% O₂ was added to the N₂O + CH₄ flow the intensity of N₂O species increased in comparison to the O₂ free experiment. This would suggest that there is less CH₄ available to react with N₂O species due to the competitive combustion reaction. The NO band at 1875 cm⁻¹ disappeared upon the addition of O₂, and an increase in the NH₄⁺ band at 1499 cm⁻¹ was seen.

The N₂O–CH₄–O₂ reaction data on reduced Gd–Pd catalyst at 300 °C showed 100% selectivity to N₂, which is in agreement with our observation in the IR spectrum. These trends continue with the change to excess oxygen by increasing the oxygen concentration from 0.3 to 4.5%. With the introduction of excess oxygen conditions, the intensity of the N₂O peaks at 2199 and 2235 cm⁻¹ further increased, again due to a loss of available CH₄ to the reduction reaction.

The final gas change of this experiment had the reaction feed turned off and the catalyst flushed under He. After flushing, the gas phase N₂O and CH₄ are no longer visible. Adsorbed dinitrogen species at 2333 cm⁻¹ and the surface NH₄⁺ groups observed at 1499 cm⁻¹ remain stable on the surface at 300 °C. The nitrate species observed at 1347 cm⁻¹ also remains on the surface after flushing.

The same DRIFTS experiment was performed over the oxidized Gd–Pd catalyst, which was inactive for NO_x reduction. Fig. 6 shows that under a flow of 1780 ppm N₂O the only observed bands were the doublet of gas phase N₂O at 2199 and 2235 cm⁻¹. With the addition of CH₄ to the feed, gas phase CH₄ was seen through bands at 3016 and 1306 cm⁻¹. The formation of new surface species with absorption bands at 1430, 1520, 1610, 1875, and a doublet around 2350 cm⁻¹ was also observed. The formation of the bands at 1430 and 1520 cm⁻¹ was observed only on the oxidized surface. The latter species was due to the formation monodentate nitrate [31–34], while the former species could arise either from CH_x or nitrogen-oxo species. The forma-

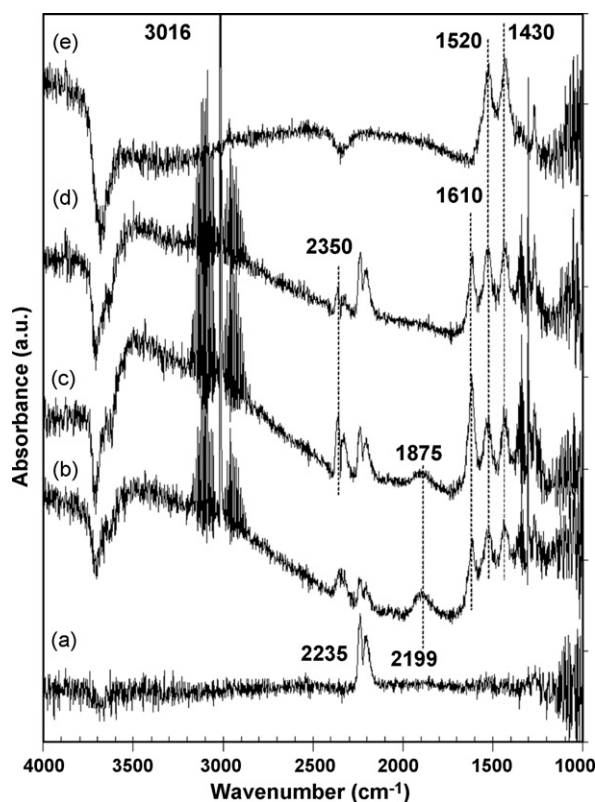


Fig. 6. DRIFT spectra taken during the sequential introduction of reactants at 300 °C to oxidized 1%Gd/2%Pd/TiO₂. (a) N₂O, (b) N₂O + CH₄, (c) N₂O + CH₄ + O₂ (low), (d) N₂O + CH₄ + O₂ (excess) and (e) He flush.

tion of nitrate in the presence of CH_4 was surprising considering that we did not observe nitrate formation under N_2O -only flow. However we could speculate that NO , observed at 1875 cm^{-1} , may be converted to nitrate species over the oxidized surface. TPD profiles following N_2O adsorption on the oxidized Gd-Pd catalyst showed a NO desorption peak at 210°C , which is lower than that observed over the reduced catalyst by 80°C . The lower desorption temperature may make conversion of NO to surface nitrate species possible. The doublet at 2350 cm^{-1} and the band at 1610 cm^{-1} indicate the presence of CO_2 and H_2O on the surface, respectively. The surface dinitrogen species observed on the reduced Gd-Pd sample is not present, which is consistent with the lack of reduction activity on the oxidized catalyst. With the addition of O_2 to the gas feed the CO_2 and H_2O band increase in intensity, due to CH_4 combustion. The other bands remain fairly constant. After the final flushing step all of the gas phase species disappear, as well as the bands of CO_2 and H_2O . Only the bands at 1430 and 1520 cm^{-1} remain.

3.5.2. NO_2 adsorption

The spectra in Figs. 7 and 8 were taken under a flow of 1780 ppm NO_2 at 300°C over oxidized and reduced Gd-Pd/ TiO_2 catalysts, respectively. Changes in surface species were monitored with time up to 35 min. Over the oxidized sample, bands at 1612 , 1577 , and 1231 cm^{-1} were formed immediately upon introduction of NO_2 . The IR band at 1612 cm^{-1} is due to the presence of bridged nitrate species, and the pair at 1578 and 1231 cm^{-1} was assigned to bidentate nitrate species [31,33,35].

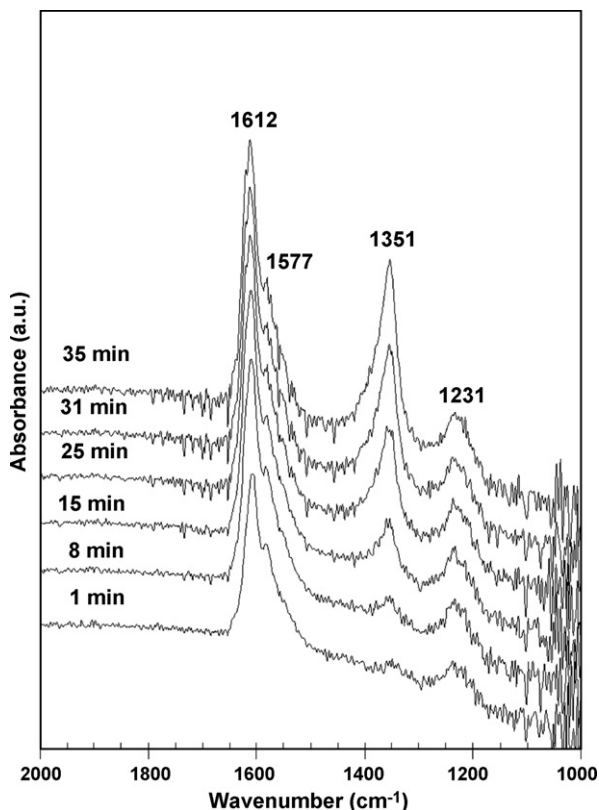


Fig. 7. DRIFT spectra of oxidized 1%Gd/2%Pd, taken as a function of time under a flow of 1780 ppm NO_2 , at 300°C .

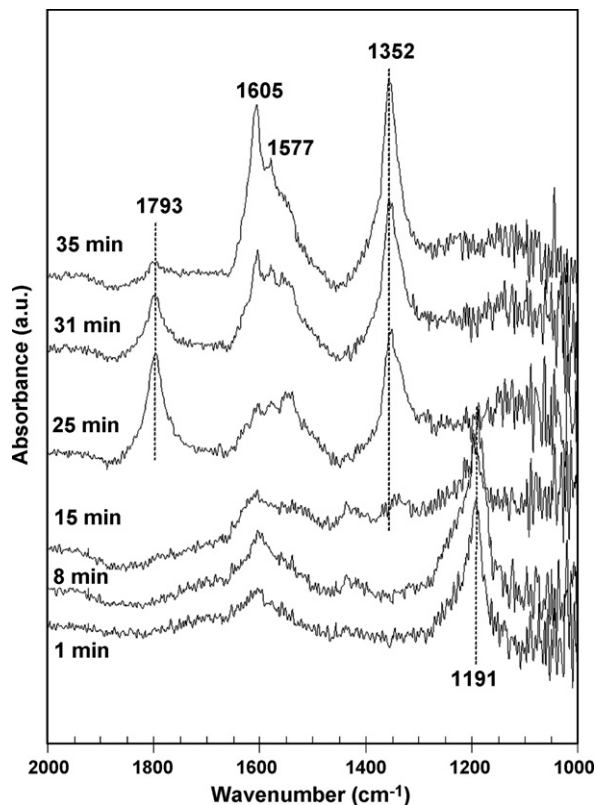


Fig. 8. DRIFT spectra of reduced 1%Gd/2%Pd, taken as a function of time under a flow of 1780 ppm NO_2 , at 300°C .

Over the first 15 min of exposure, these bands increased in intensity and thereafter remained constant. The species observed at 1351 cm^{-1} lags behind in forming on the surface, but increases in intensity with exposure time. Vibrational frequencies in this region are typical of nitro (NO_2^-) species [33,36].

On the reduced Gd-Pd catalyst, the spectrum taken after 1 min of exposure showed bands at 1605 and 1191 cm^{-1} . A band in the region of 1605 cm^{-1} is due to bridged nitrate species as on the oxidized sample, though in comparison, the intensity was much smaller over the reduced sample. The band at 1191 cm^{-1} corresponds to molecularly adsorbed NH_3 on Lewis acid sites. The ammonia formation could be due to a reaction between NO_2 and chemisorbed hydrogen that was left on the surface after the in situ reduction step. This band decreases with time as the adsorbed NH_3 is removed from the surface. Between 25 and 35 min, the development of bridged nitrate (1605 cm^{-1}), bidentate nitrate (1577 cm^{-1}), and nitro species (1352 cm^{-1}) are observed. The growth of these bands corresponds to the appearance and removal of linear adsorbed NO on Pd^+ characterized by a band at 1793 cm^{-1} . Linear NO adsorption on Pd has been studied on single crystals as well as supported catalysts [37–43]. Previously, we concluded that the 1793 cm^{-1} band indicated linear NO adsorption on partially reduced Pd sites (Pd^+) [22]. This evolution of surface species results in spectra similar to those observed over the oxidized catalyst, which indicated that the catalyst surface was oxidized as the duration of NO_2 exposure increased, perhaps making more lattice oxygen available for bridged and bidentate nitrate formation. Reduction in the inten-

sity of Pd–NO suggests that reduced Pd sites are less available due to complete oxidation of Pd in the presence of NO_2 .

3.5.3. $\text{NO}_2 \rightarrow \text{NO}_2 + \text{CH}_4 \rightarrow \text{NO}_2 + \text{CH}_4 + \text{O}_2$ adsorption

DRIFT spectra were taken over oxidized and reduced Gd-Pd/TiO₂ catalysts following exposure to NO_2 , $\text{NO}_2 + \text{CH}_4$, $\text{NO}_2 + \text{CH}_4 + \text{O}_2$ (low O_2 concentration), and $\text{NO}_2 + \text{CH}_4 + \text{O}_2$ (high O_2 concentration) flows in sequence. Feed concentrations were $\text{NO}_2 = 1780$ ppm, $\text{CH}_4 = 2.13\%$, $\text{O}_2 = 0.3$ and 4.5% . Spectra were taken after the catalysts were exposed to each gas mixture for 30 min at a surface temperature of 300°C .

The high and low wavenumber regions for the oxidized sample are shown in Figs. 9 and 10. Upon the introduction of NO_2 , bands at 1605 , 1577 , and 1222 cm^{-1} were observed, corresponding to bridged and bidentate nitrates as in the previous experiment. A surface nitro species at 1349 cm^{-1} is also observed. With the addition of CH_4 to the gas feed the bridged and bidentate species decrease in intensity while an increase in the nitro band occurs. Concurrently, bands at 3016 and 1304 cm^{-1} are observed due to gas phase CH_4 . Multiplets in the 3200 to 3400 cm^{-1} region and a band at 1191 cm^{-1} also appeared. The multiplets corresponded to N–H stretching of coordinatively adsorbed NH_3 , and the 1191 cm^{-1} band is a characteristic frequency of $\text{NH}_{3\text{sy}}$ coordinated to Lewis acid sites. The formation of NH_x species suggested that activation of CH_4 was achieved on the oxidized catalyst, possibly through hydrogen abstraction at bridged/bidentate nitrate sites. Previously, for the NO-CH_4 -

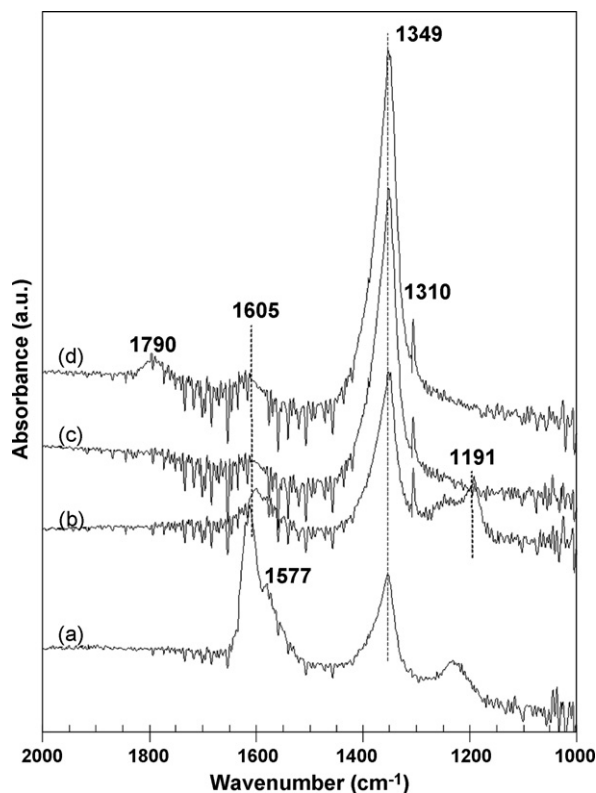


Fig. 9. DRIFT spectra taken during the sequential introduction of reactants at 300°C to oxidized $1\%\text{Gd}/2\%\text{Pd}/\text{TiO}_2$. (a) NO_2 , (b) $\text{NO}_2 + \text{CH}_4$, (c) $\text{NO}_2 + \text{CH}_4 + \text{O}_2$ (low), (d) $\text{NO}_2 + \text{CH}_4 + \text{O}_2$ (excess). Low wavenumber region.

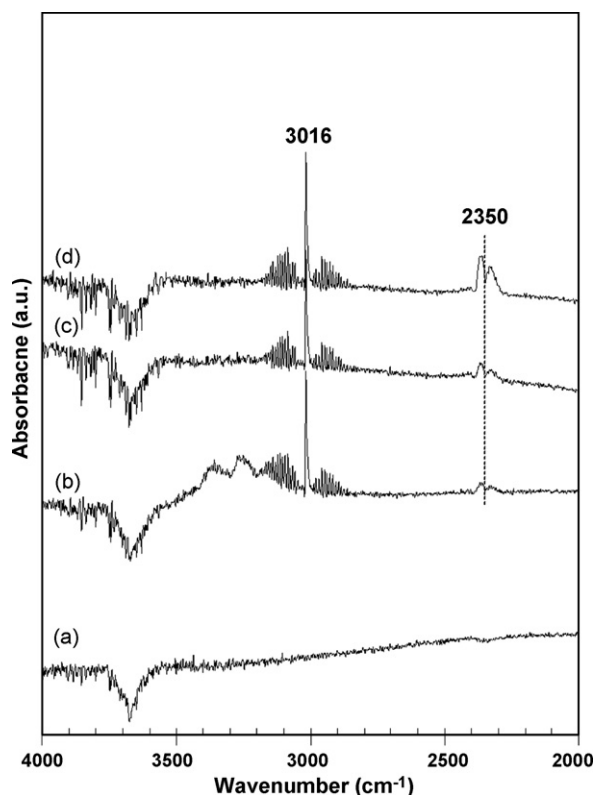


Fig. 10. DRIFT spectra taken during the sequential introduction of reactants at 300°C to oxidized $1\%\text{Gd}/2\%\text{Pd}/\text{TiO}_2$. (a) NO_2 , (b) $\text{NO}_2 + \text{CH}_4$, (c) $\text{NO}_2 + \text{CH}_4 + \text{O}_2$ (low) and (d) $\text{NO}_2 + \text{CH}_4 + \text{O}_2$ (excess). High wavenumber region.

O_2 reaction over the oxidized Gd-Pd/TiO₂ catalyst we did not observe the formation of NH_x species, indicating that activation of CH_4 was not possible on the oxidized catalyst after exposure to NO [22]. The formation of bridged/bidentate nitrate was significantly less after NO exposure than from NO_2 exposure on the catalyst. This seems to support our supposition that CH_4 could be activated on NO_2 covered Gd-Pd/TiO₂ to form CH_x and dissociated hydrogen, which further react with nitrogen-oxo species on the surface to form NH_x . CH_4 activation through adsorbed NO_2 has been reported in the literature [23–26,44]. Over Co-FER, Li and Armor proposed a mechanism that involves the formation of adsorbed NO_2 on Co^{2+} sites as the first step, followed by CH_4 activation by the adsorbed NO_2 to CH_3^\bullet radicals. The CH_3^\bullet radical could react with bound NO_2 to form nitromethane (CH_3NO_2), which further can react with gas phase NO to N_2 , H_2O , and CO_2 (23). Hall and co-workers investigated the role of free CH_3^\bullet radicals over Co-ZSM-5 and H-ZSM-5 catalysts and proposed that after the oxidation of NO to NO_2 , CH_3^\bullet free radicals, formed by interaction with NO_2 , react with NO_x and O_2 [20].

When low concentrations of O_2 were introduced (3000 ppm) to the $\text{NO}_2 + \text{CH}_4$ flow, disappearance of NH_x species was observed, suggesting that the species is easily oxidized in the presence of oxygen. This corresponded to a significant increase in the intensity of nitro species at 1349 cm^{-1} . Adsorbed CO_2 was also observed through a doublet centered near 2350 cm^{-1} .

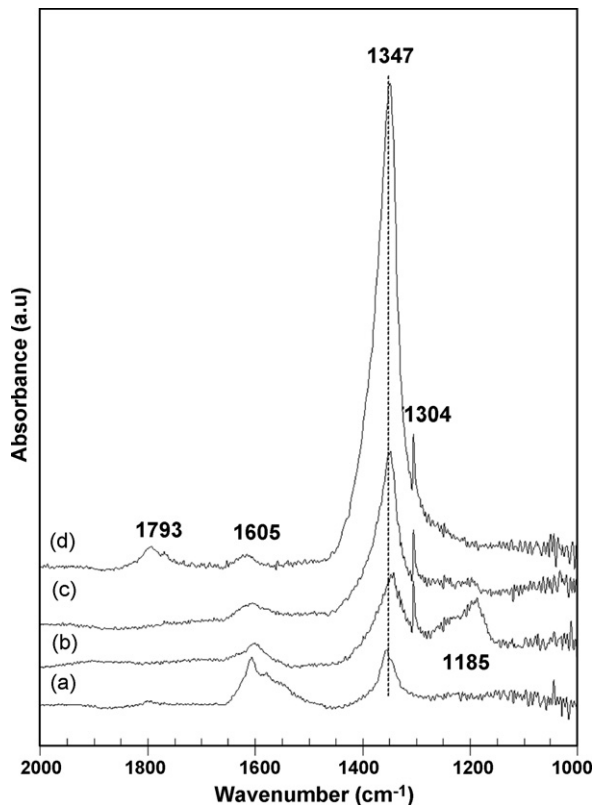


Fig. 11. DRIFT spectra taken during the sequential introduction of reactants at 300 °C to reduced 1%Gd/2%Pd/TiO₂. (a) NO₂, (b) NO₂ + CH₄, (c) NO₂ + CH₄ + O₂ (low) and (d) NO₂ + CH₄ + O₂ (excess). Low wavenumber region.

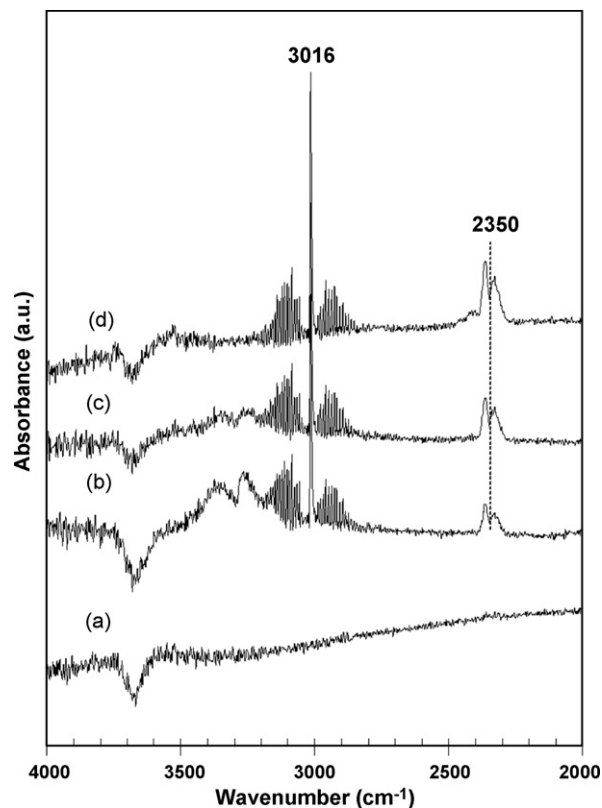


Fig. 12. DRIFT spectra taken during the sequential introduction of reactants at 300 °C to reduced 1%Gd/2%Pd/TiO₂. (a) NO₂, (b) NO₂ + CH₄, (c) NO₂ + CH₄ + O₂ (low) and (d) NO₂ + CH₄ + O₂ (excess). High wavenumber region.

Figs. 11 and 12 present the results from the sequential introduction performed on the reduced catalyst. Under NO₂ flow only, the intensity of bridged nitrate and nitro species were similar to the oxidized sample. Additionally only a small band at 1789 cm⁻¹ associated with Pd–NO was seen, suggesting that most of the Pd sites were oxidized. When methane was introduced we again observed the formation of NH_x species at 3200–3400 cm⁻¹ and 1185 cm⁻¹, the appearance of CH₄ at 3016 and 1304 cm⁻¹, and an intensity decrease of bridged nitrate species. This consistent evidence strengthens our proposed CH₄–nitrate interaction. Under the low O₂ feed the ammonia species disappear, which coincides with an increase in nitro groups at 1347 cm⁻¹. A strong CO₂ band is observed, and these trends continue with increased O₂ concentration.

3.6. In situ DRIFTS during reaction of NO₂ + CH₄ + O₂ at different temperatures

DRIFTS spectra were taken over reduced Gd–Pd/TiO₂ during reaction of 1780 ppm NO₂, 2.13% CH₄, and 3000 ppm O₂ in balance He, at temperatures of 25, 75, 150, 225, and 300 °C (Figs. 13 and 14). At low temperatures bridged nitrate at 1610 cm⁻¹, bidentate nitrate at 1581/1240 cm⁻¹, and monodentate nitrito at 1486 cm⁻¹ were observed. With increasing reaction temperature a decrease in bidentate nitrate and monodentate nitrito species occurred, along with the formation of

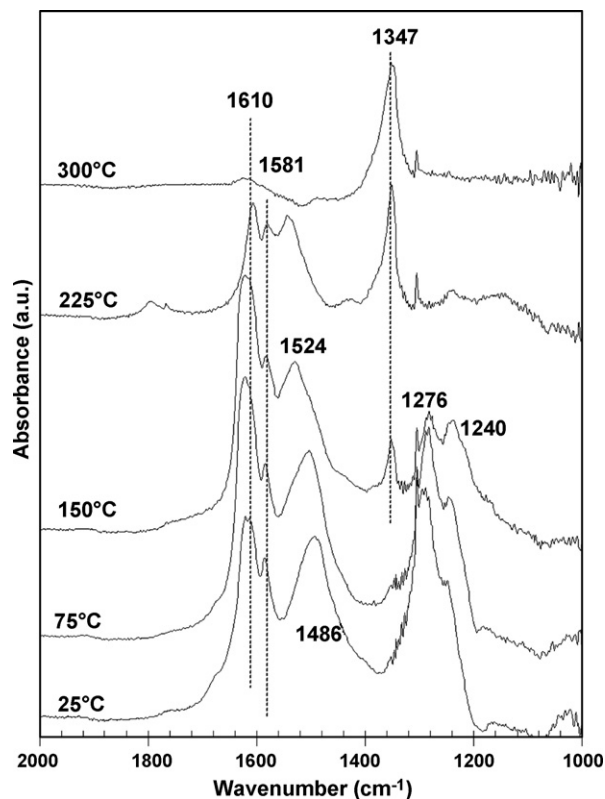


Fig. 13. In situ DRIFT spectra of reduced 1%Gd/2%Pd/TiO₂ during reaction. Low wavenumber region.

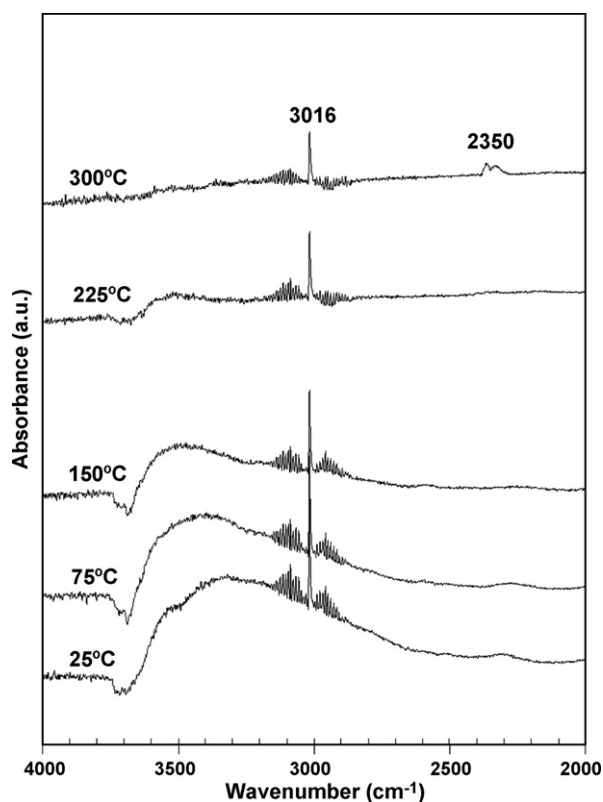


Fig. 14. In situ DRIFT spectra of reduced 1%Gd/2%Pd/TiO₂ during reaction. High wavenumber region.

monodentate nitrate species with a band at 1524 cm⁻¹ and nitro species at 1347 cm⁻¹ (28–29). At 300 °C all the nitrate species in the 1450–1625 cm⁻¹ range disappeared and CO₂ was observed around 2350 cm⁻¹. These changes indicate light off of the reduction reaction, and support the conclusion of CH₄ activation through interaction with surface nitrate species.

4. Conclusions

The versatility of Gd–Pd/TiO₂ catalyst for reduction of not only NO but also other nitrogen oxides (N₂O and NO₂) with methane has been demonstrated. Consistent with previous results, the bimetallic Gd–Pd/TiO₂ catalyst was shown to maintain the Pd sites in metallic state in higher O₂ concentrations compared to the Gd-free catalysts, retaining activity for NO_x reduction. As suggested previously (17, 20, 21, 22) the highly electropositive nature of Gd may be primary reason for this phenomenon. Mechanistic studies of the N₂O reduction suggest a role for an intermediate NH⁴⁺ species resulting in the appearance of adsorbed dinitrogen. Although DRIFT spectra show that the catalyst is partially oxidized under a flow of NO₂, under reaction conditions this may not be the case. Post reaction XPS shows that 40% of Pd remains in the active metallic state even after exposure to NO₂ and in an O₂ rich feed. Furthermore comparisons of in situ DRIFTS results yield very similar spectra when the reaction is performed over both the oxidized and reduced catalyst. As with the reduction of NO, the reduction

of NO₂ seems to proceed through the interaction of CH₄ with surface bidentate nitrates. However, under reaction conditions nitro species, not linearly adsorbed NO, are the dominant surface species.

Acknowledgments

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