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In Situ FTIR Studies of the Selective Catalytic Reduction of NO by C_3H_6 over Pt/Al_2O_3

Dinyar K. Captain and Michael D. Amiridis

Department of Chemical Engineering, University of South Carolina, Columbia, South Carolina 29208
E-mail: amiridis@engr.sc.edu

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The selective catalytic reduction (SCR) of nitric oxide (NO) by propylene (C_3H_6) over a 0.8 wt% Pt/Al_2O_3 catalyst was studied by the use of *in situ* Fourier transform infrared (FTIR) spectroscopy. Spectra of both the Pt/Al_2O_3 catalyst as well as the bare Al_2O_3 support were collected during the course of this study. NO adsorption resulted in the formation of nitrate species associated with the Al_2O_3 support, as well as surface NO species associated with Pt. Similarly, C_3H_6 adsorption resulted in the formation of carboxylate species associated with Al_2O_3, as well as surface CO associated with Pt. Finally, experiments conducted with the reactive NO–C_3H_6–O_2 mixture resulted in the formation of surface cyanide (–CN) and isocyanate (–NCO) species. The origin and reactivity of these species is discussed in view of their potential involvement as intermediates in the hydrocarbon–SCR reaction. © 1999 Academic Press

Key Words: **selective catalytic reduction; nitric oxide; propylene; platinum; infrared spectroscopy.**

INTRODUCTION

NO_x emissions are today regulated through a complex network of federal and local laws (1). The selective catalytic reduction (SCR) of nitric oxide by ammonia over vanadia-based catalysts and the nonselective reduction of NO by carbon monoxide and unburned hydrocarbons over noble metal-based three way catalysts are currently used for the control of NO_x emissions from stationary and mobile sources, respectively. The potential use of hydrocarbons as reducing agents in the selective catalytic reduction of nitric oxide has certain advantages over both processes (2), and this is why this reaction has received a lot of attention since it was introduced in 1991 (3, 4).

Cu-containing ion exchanged zeolites, and in particular, Cu–ZSM5, have been the focus of several studies due to their high initial activity (3, 4). These catalysts suffer, however, from low hydrothermal stability in realistic exhaust compositions and undesirable selectivities toward carbon monoxide (5–8). Supported platinum-based catalysts are also active for NO_x reduction, but at lower temperatures (2, 9–15), and are not significantly affected by the presence of water (2, 3, 12, 16) in the exhaust stream. Limitations to their commercial utilization are caused by the narrow temperature window of operation and their significant selectivities toward nitrous oxide (N_2O) (2, 9–15, 17).

Given the commercial potential of platinum-based HC–SCR catalysts, more attention has focused recently on their performance (2, 4–5, 9–17). There is still a limited understanding, however, of the fundamental surface chemistry involved in this reaction. This study aims toward this understanding and complements kinetic studies conducted with the same catalyst (9). *In situ* FTIR spectra were collected at 250°C. The kinetic results indicate that at this temperature the catalyst is active but has not yet reached its maximum activity. Spectra were collected at atmospheric pressure over both the Pt/Al_2O_3 catalyst and the bare alumina support, under a variety of gas compositions. Isotopic studies with labeled nitric oxide (^{15}NO) were also used to further qualify the identification of the surface species present.

EXPERIMENTAL

Catalyst Preparation

The 0.8 wt% Pt/Al_2O_3 catalyst was prepared by incipient wetness impregnation of the γ-Al_2O_3 support (Vista Chemical Co.) with an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ (Aldrich Chemical Co.). Prior to impregnation the support was calcined overnight at 500°C in air. Following impregnation, the sample was dried at 120°C for 2 h and then calcined in air for 5 h at 500°C. The calcined catalyst had a BET surface area of 147 m^2/g and a Pt loading of 0.81 wt% (ICP-Galbraith Laboratories). Hydrogen chemisorption measurements indicate that the Pt was fully (i.e., 100%) dispersed on the alumina support.

Infrared Spectroscopy

Infrared spectra were collected using a Nicolet 740 Fourier transform infrared (FTIR) spectrometer equipped with an MCT-B detector. Transmission spectra were collected in the single beam mode with a resolution of 2 cm^{-1}. Reference spectra of the clean surfaces in flowing He were collected separately and difference spectra between the

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samples and the corresponding reference are shown herein. A stainless steel IR cell with NaCl windows cooled by flowing water and a 10-cm path length was used. A heating element wrapped around the cell allowed collection of *in situ* spectra at 250 and 350°C. The temperature was monitored through a thermocouple located in the cell and in close proximity with the catalyst sample.

Catalyst samples were prepared as self-supported wafers, 12 mm in diameter and with a "thickness" of about 20 mg/cm^2. Prior to each experiment the samples were pretreated at 250°C in a flowing 2% O_2 in He mixture for 2 h. Certified analyzed mixtures of 1.0% NO in He (Matheson), 1.0% NO_2 in He (Scott Specialty Gases), 1.0% C_3H_6 in He, 10.0% O_2 in He, and a 99.9999% He carrier gas (National Specialty Gases; further purified by an oxygen trap) were used to prepare the different gas mixtures; typical concentrations used were 2000 ppm of NO/NO_2 and C_3H_6, and 2.0% of O_2. Gases were mixed at the appropriate amounts by the use of a system of needle valves and flow meters and preheated prior to the introduction to the cell. The volumetric flow rate of the gas mixtures was held constant at 100 cm^3/min.

RESULTS AND DISCUSSION

NO Adsorption

Al_2O_3. The spectrum of the alumina support, following exposure to a mixture of 2000 ppm NO in He at 250°C for 20 min, is shown in Fig. 1a. In addition to the gas phase NO (doublet at 1906 and 1851 cm^{-1}), the spectrum

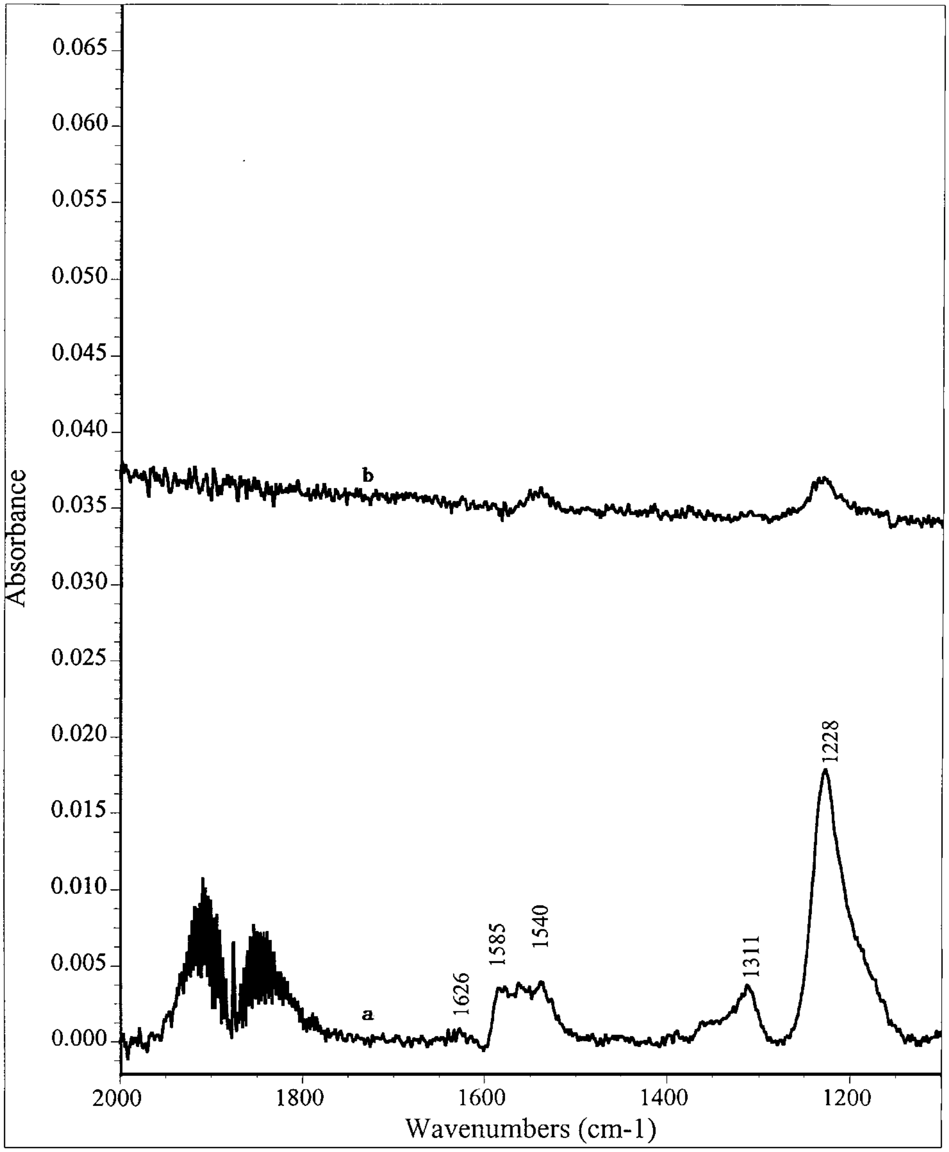

FIG. 1. *In situ* infrared spectra at 250°C of an initially oxidized Al_2O_3 support: (a) exposure to 2000 ppm NO in He for 20 min; (b) flushing of (a) with He for 10 min.

indicates the formation of adsorbed species with characteristic IR peaks in the 1200–1650 cm^{-1} range. These include features at 1626, 1311, and 1228 cm^{-1} and a broad triplet between 1585 and 1540 cm^{-1} and can be assigned to nitrates ($-NO_3^-$) adsorbed on the alumina surface (18–22), including bidentate-type species with characteristic peaks at 1585 and 1228 cm^{-1}. Very similar results have been observed during NO_2 adsorption on alumina (22). The formation of NO_2 as a precursor to the nitrates observed in our studies may be attributed to oxygen which is present on the alumina surface as a result of the oxidation pretreatment in our protocol. When NO was removed from the gas phase and the cell was flushed with He, the intensity of the nitrate peaks decreased significantly (Fig. 1b), indicating that these species are not strongly adsorbed.

Pt/Al_2O_3. The adsorption of NO was also carried on the Pt/Al_2O_3 catalyst with the results shown in Fig. 2a. In addition to the peaks due to the nitrates associated with the alumina support, a new peak was also observed at 1740 cm^{-1}. This peak can be assigned to a nitrosium ion ($-NO^-$) linearly adsorbed on Pt (18, 19, 23). The presence of 2% O_2 in the gas phase during the adsorption of NO resulted in an increased formation of NO_2 and, subsequently, a significant increase in the intensity of the peaks assigned to adsorbed nitrates. On the contrary, the peak at 1740 cm^{-1},

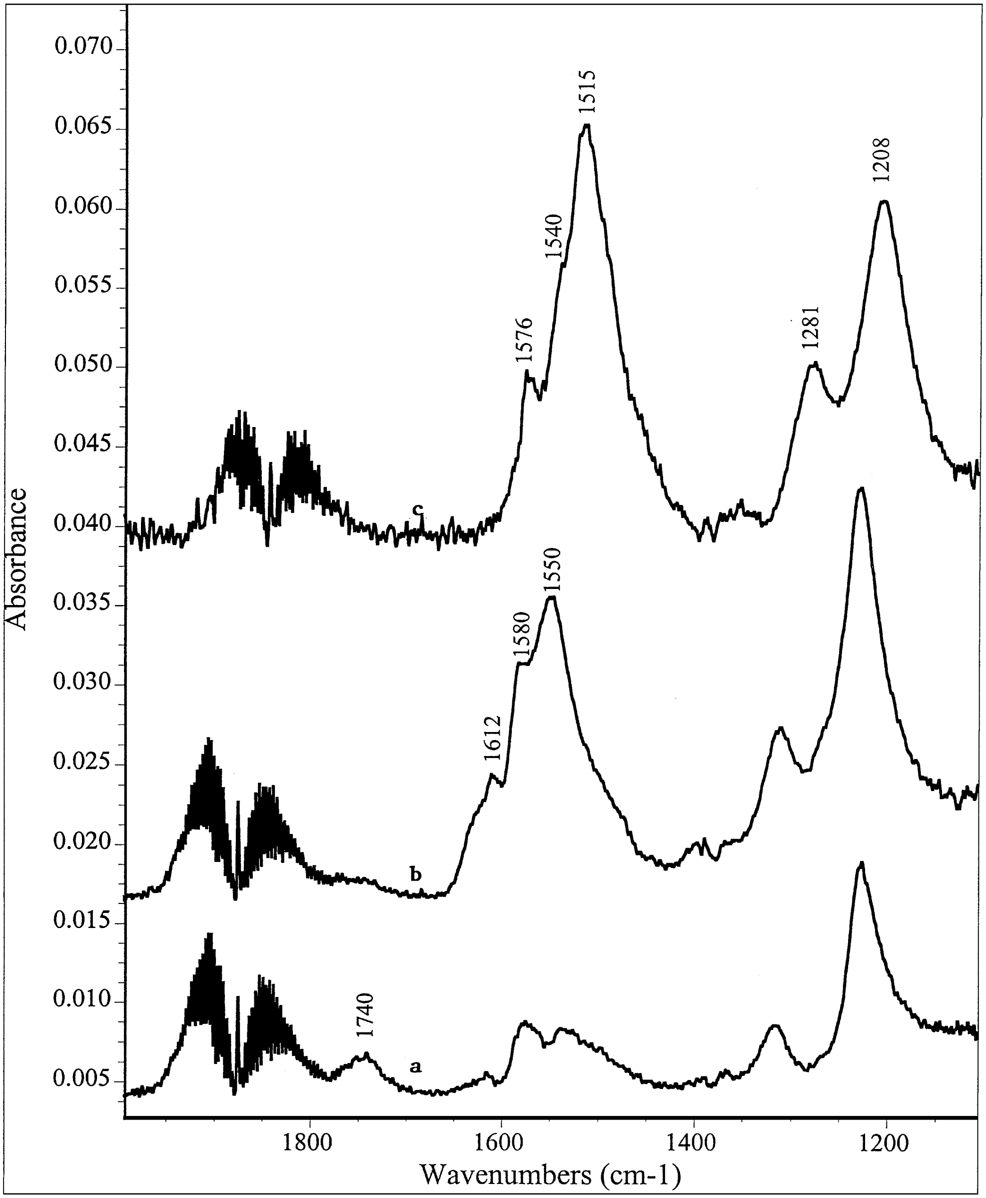

FIG. 2. *In situ* infrared spectra at 250°C of an initially oxidized Pt/Al_2O_3 catalyst: (a) 2000 ppm NO in He for 20 min; (b) 2000 ppm NO, 2% O_2 in He for 20 min; (c) 2000 ppm ^{15}NO, 2% O_2 in He for 20 min.

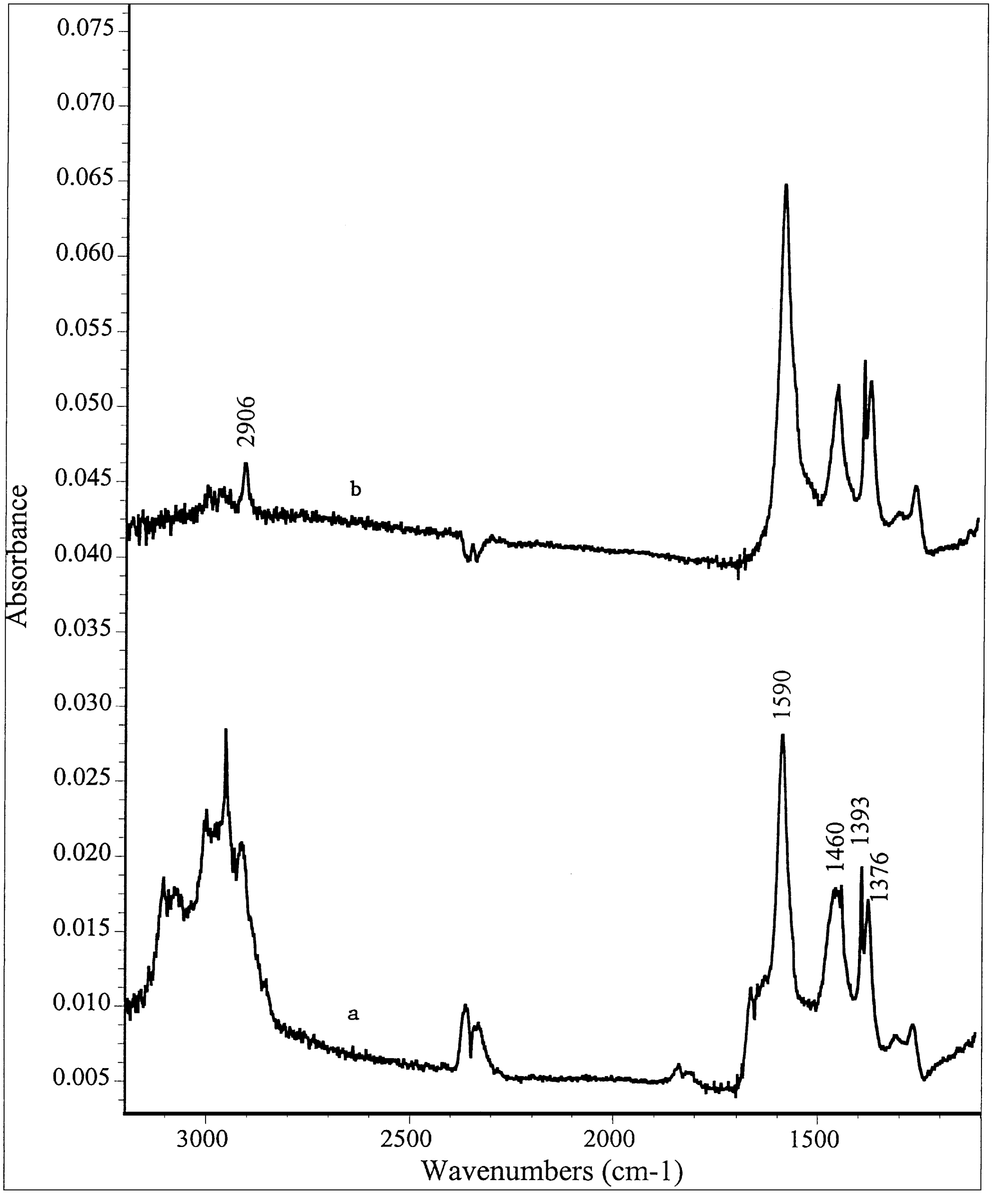

FIG. 3. *In situ* infrared spectra at 250°C of an initially oxidized Al_2O_3 support: (a) 2000 ppm C_3H_6 in He for 1 h; (b) flushing of (a) with He for 30 min.

corresponding to the nitrosium ion, was no longer present, suggesting that this species is not stable in the presence of oxygen.

Finally, when $^{15}NO + O_2$ was flowed over the Pt/Al_2O_3 catalyst (Fig. 2c), the peaks at 1612, 1580, 1550, 1311, and 1228 cm^{-1} were shifted to 1576, 1540, 1515, 1281, and 1208 cm^{-1}, respectively, as expected by the proposed assignments.

C_3H_6 Adsorption

Al_2O_3. The spectrum of the alumina support, following exposure to a mixture of 2000 ppm C_3H_6 in He at 250°C for 1 h is shown in Fig. 3a. Six distinct peaks can be seen at 1590, 1460, 1393, 1376, 1312, and 1266 cm^{-1}. These can be assigned to adsorbed carboxylates ($-COO^-$) in agreement with previous literature reports (21, 24–26). IR peaks at 1590, 1380, and 1395 cm^{-1} have been previously assigned to adsorbed formate ions on alumina and are attributed to the asymmetric and symmetric $-COO^-$ stretching vibrations and the –CH bending vibrations, respectively (25). The peak at 1460 cm^{-1} can be assigned to the vibration of an adsorbed acetate species in agreement with previous reports (26). This assignment is addressed further in the next section. The weaker peaks at 1312 and 1266 cm^{-1} can be also assigned to surface acetates and are characteristic of

out of plane –CH bending and C–C stretching vibrations, respectively (26). In addition, a set of peaks in the 2900–3100 cm^{-1} region observed in Fig. 3a is due to the stretching vibrations of the gas phase propylene present in the IR cell. The corresponding bending vibrations are present in the 1400–1700 cm^{-1} region and appear as shoulders in the spectrum of Fig. 3a. When the cell was flushed with He (Fig. 3b), the gas phase peaks disappeared revealing the presence of an adsorbed species with a characteristic IR peak at 2906 cm^{-1}. This region is typical of –CH stretching and the corresponding species is believed to be an adsorbed hydrocarbon fragment (25–28). The intensity of the carboxylate peaks remained constant during flushing with either He or an O_2/He mixture, indicating that these species are stable under these conditions.

Pt/Al_2O_3. The adsorption of C_3H_6 was also carried on the Pt/Al_2O_3 catalyst with the results shown in Fig. 4. Similar to the spectrum of the alumina support exposed to C_3H_6, the spectrum of the Pt/Al_2O_3 catalyst includes several carboxylate peaks in the 1250–1600 cm^{-1} region. The intensity of these peaks however, is significantly higher in the case of Pt/Al_2O_3. This can be attributed to the catalytic properties of Pt for the oxidation of C_3H_6 and the presence of surface

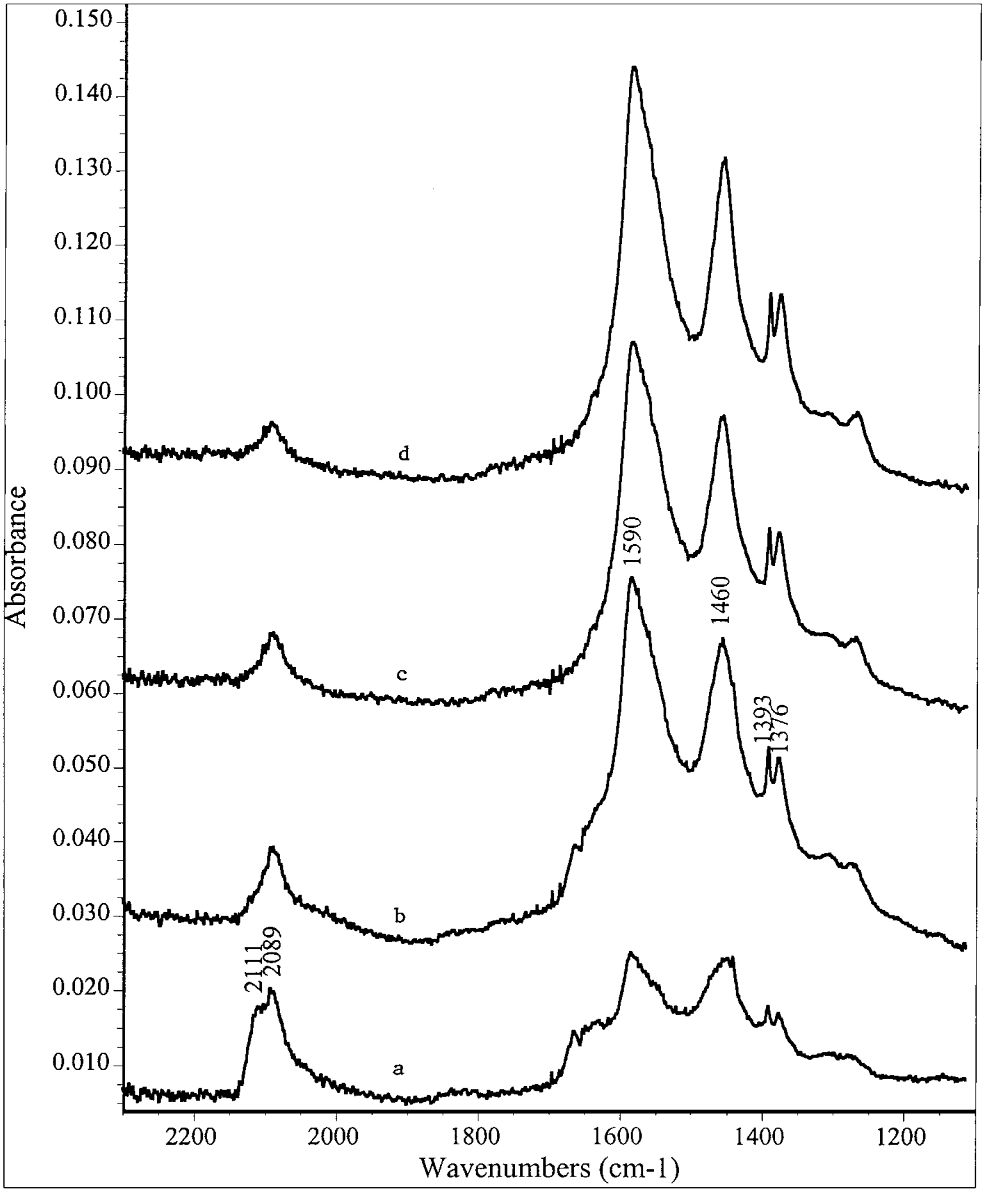

FIG. 4. *In situ* infrared spectra at 250°C of an initially oxidized Pt/Al_2O_3 catalyst: (a) 2000 ppm C_3H_6 in He for 15 min; (b) 2000 ppm C_3H_6 in He for 1 h; (c) flushing of (b) with He for 30 min; (d) flushing of (c) with 2% O_2/He for 30 min.

oxygen (as a result of the pretreatment of the catalyst), which results in increased carboxylate formation. In addition, a new doublet is also noticed at 2111 and 2089 cm^{-1}. This doublet appears immediately following exposure of the catalyst to C_3H_6 (Fig. 4a), but its intensity decreases with time on stream. After a period of 1 h the 2111 cm^{-1} peak disappears leaving a well-defined peak at 2089 cm^{-1} (Fig. 4b). IR peaks in this region have been previously assigned to CO species adsorbed on Pt (29–30). In particular, a peak at 2080 cm^{-1} has been assigned to –CO linearly bonded to a reduced Pt atom, while a peak at 2120 cm^{-1} has been assigned to a –CO species which is bonded to a Pt atom with an oxygen adsorbed on it, i.e., as would be the case when the catalyst is oxidized. CO bonded to a reduced metal atom is commonly assumed to be attached more strongly than CO bonded to the oxidized metal (31). Initially, a significant portion of the Pt in the Pt/Al_2O_3 catalyst may be oxidized as a result of the pretreatment in flowing O_2. Reduction of the platinum by propylene can account for the gradual disappearance of the peak at 2111 cm^{-1} with increased time on stream.

When the cell was flushed with He (Fig. 4c), a slight decrease in the intensity of the CO peak at 2089 cm^{-1} was observed, while the carboxylate peaks were unaffected indicating the strong stability of these species. When the cell was flushed with 2% O_2 in He (Fig. 4d), the intensity of the CO peak decreased further, but once again no significant changes were observed in the carboxylate region.

The addition of 2% O_2 to the gas phase during the adsorption of C_3H_6 results in a very significant increase in the intensity of the carboxylate peaks (Fig. 5b). This increase can be attributed to the catalytic activity of Pt for the oxidation of C_3H_6 and is in agreement with our kinetic studies (9, 10), which show that in the absence of NO from the gas phase, there is a high rate of C_3H_6 oxidation under these conditions. In addition to the carboxylate peaks, the peaks attributed to adsorbed CO in the 2100 cm^{-1} region are also present at an increased intensity.

When C_3H_6 was removed from the gas phase and He was flowed over the sample of Fig. 5b, once again no significant changes were observed in the carboxylate region (Fig. 5c). When the sample was heated, however, to 350°C in a flowing stream of He, significant changes were noticed (Fig. 5d). In particular, two strong peaks are present at 1568 and 1460 cm^{-1}, while the peaks responsible for the formate species at 1590, 1393, and 1377 cm^{-1} are no longer present. Identical behavior of surface carboxylates was observed during propylene and acetone adsorption on V_2O_5/TiO_2 by Busca *et al.* (26). These authors assigned the two peaks at 1568 and 1460 cm^{-1} to the $–COO^-$ stretching vibrations of adsorbed acetate species. Thus, we can conclude that propylene adsorption at 250°C results in the formation of a mixture of surface formates and acetates. Only the acetates, which are known to be more stable, can withstand the higher temperatures of 350°C while the formates decompose under these conditions.

Reaction Studies

The IR spectrum collected during the exposure of the Pt/Al_2O_3 catalyst to a 2000 ppm NO–2000 ppm C_3H_6–2% O_2 mixture at 250°C is shown in Fig. 6a. This spectrum contains strong peaks in the carboxylate region (1200–1650 cm^{-1}) and an additional broad peak centered at approximately 2158 cm^{-1} with a shoulder at 2250 cm^{-1}. When ^{15}NO was used (Fig. 6b), the peak at 2158 cm^{-1} shifted to 2130 cm^{-1} indicating the presence of N in the corresponding species. In agreement with previous literature reports, this peak can be assigned to an adsorbed cyanide (–CN) species (24, 32). The shoulder at 2250 cm^{-1} can be assigned to an adsorbed isocyanate species (–NCO), in agreement with earlier studies conducted during the investigation of the CO–NO reaction (33–35). The presence of an isocyanate reaction intermediate has been also recently proposed for the HC–SCR reaction (24, 32). The use of labeled ^{15}NO resulted in a shift of the shoulder from 2250 to 2232 cm^{-1}, in support of the proposed assignment.

The spectrum of the catalyst collected following removal of the reacting gas mixture and flushing of the cell with He is shown in Fig. 6c. With the exception of the isocyanate peak at 2250 cm^{-1}, the intensities of all other peaks remain essentially unaffected, suggesting that the cyanide and carboxylate species are strongly adsorbed on the catalyst surface under these conditions.

The spectrum of the Pt/Al_2O_3 catalyst under reaction conditions at 350°C is shown in Fig. 6d. Kinetic experiments (9, 10) have shown that this temperature is above the temperature of maximum NO reduction, and, hydrocarbon combustion reaches 100%. In comparison to the spectrum collected at 250°C (Fig. 6a), a significant decrease in the intensity of the cyanide peak at 2158 cm^{-1} is observed. The isocyanate (2250 cm^{-1}) peak is barely visible, but still present under these conditions. The carboxylate region is also significantly different in accordance with the discussion in the previous section on the different types of carboxylates and their relative stability. While at 250°C a mixture of surface formates and acetates are present on the catalyst, at 350°C only the acetates are observed. Once again, when the cell was flushed with He, only the intensity of the isocyanate peak was affected.

Finally, the NO–C_3H_6 reaction was also carried out in the absence of O_2 at 250 and 350°C (Figs. 7a and 7b). Kinetic measurements (9) have shown that the reduction of NO does not proceed at significant rates under these conditions. At both temperatures carboxylate and cyanide species are present on the catalyst surface. On the contrary, there is no evidence for the presence of the isocyanate species. In contrast to the results obtained in the presence of oxygen, in this case the intensity of the cyanide peak is significantly

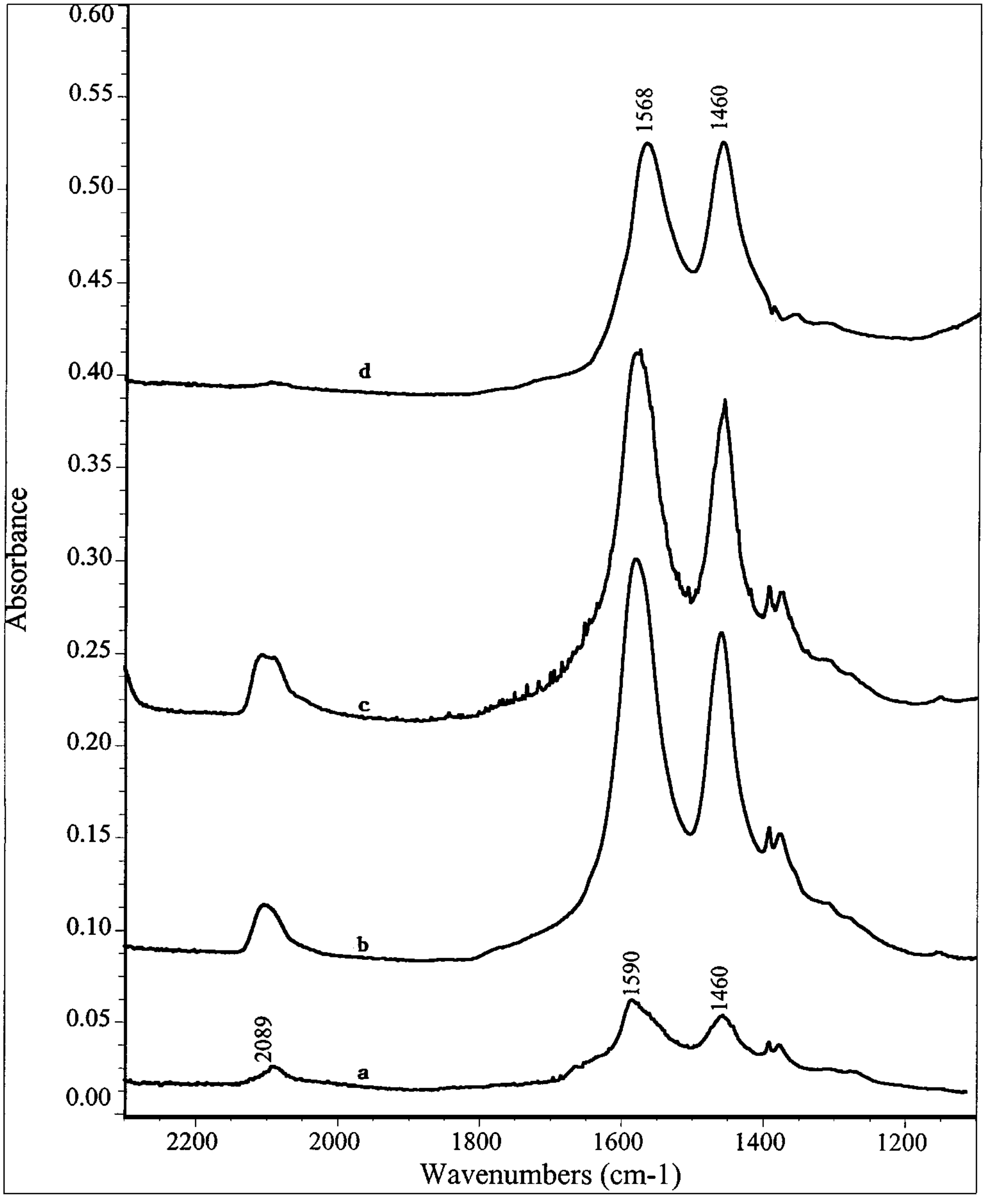

FIG. 5. *In situ* infrared spectra at 250°C for of an initially oxidized Pt/Al_2O_3 catalyst: (a) 2000 ppm C_3H_6 in He for 1 h; (b) 2000 ppm C_3H_6, 2% O_2 in He for 15 min; (c) flushing of (b) with He for 20 min; (d) heating of (c) to 350°C and flushing with He for 5 min.

higher at 350°C and almost equals the intensity of the main carboxylate peaks. Once again surface acetates are favored over the formates at the higher temperature, although in the absence of oxygen small amounts of the formates are still present at 350°C. Upon flushing of the cell with He at 350°C, the formates decompose, while the cyanide and acetate groups are stable, in agreement with our previous results.

Reactivity and Origin of Cyanide and Isocyanate

To further investigate the stability and reactivity of the surface cyanide and isocyanate species, studies were conducted with the HC–SCR reactants being flowed over surfaces containing these species. When either He, O_2/He, NO/He, NO/O_2/He, or NO_2/He was flowed over the surfaces corresponding to the spectra of Figs. 6a and 7a, no decrease was observed in the intensity of the cyanide peak at 2158 cm^{-1}. This indicates that the surface cyanide does not react toward the formation of an N–N containing species and is probably a spectator byproduct of the HC–SCR reaction.

Several spectra of a Pt/Al_2O_3 catalyst exposed to NO/C_3H_6/O_2/He reacting mixtures at 250°C after a period of 3 min are shown as Figs. 8.1a through 8.6a. This short time on stream was chosen for the study of the reactivity of

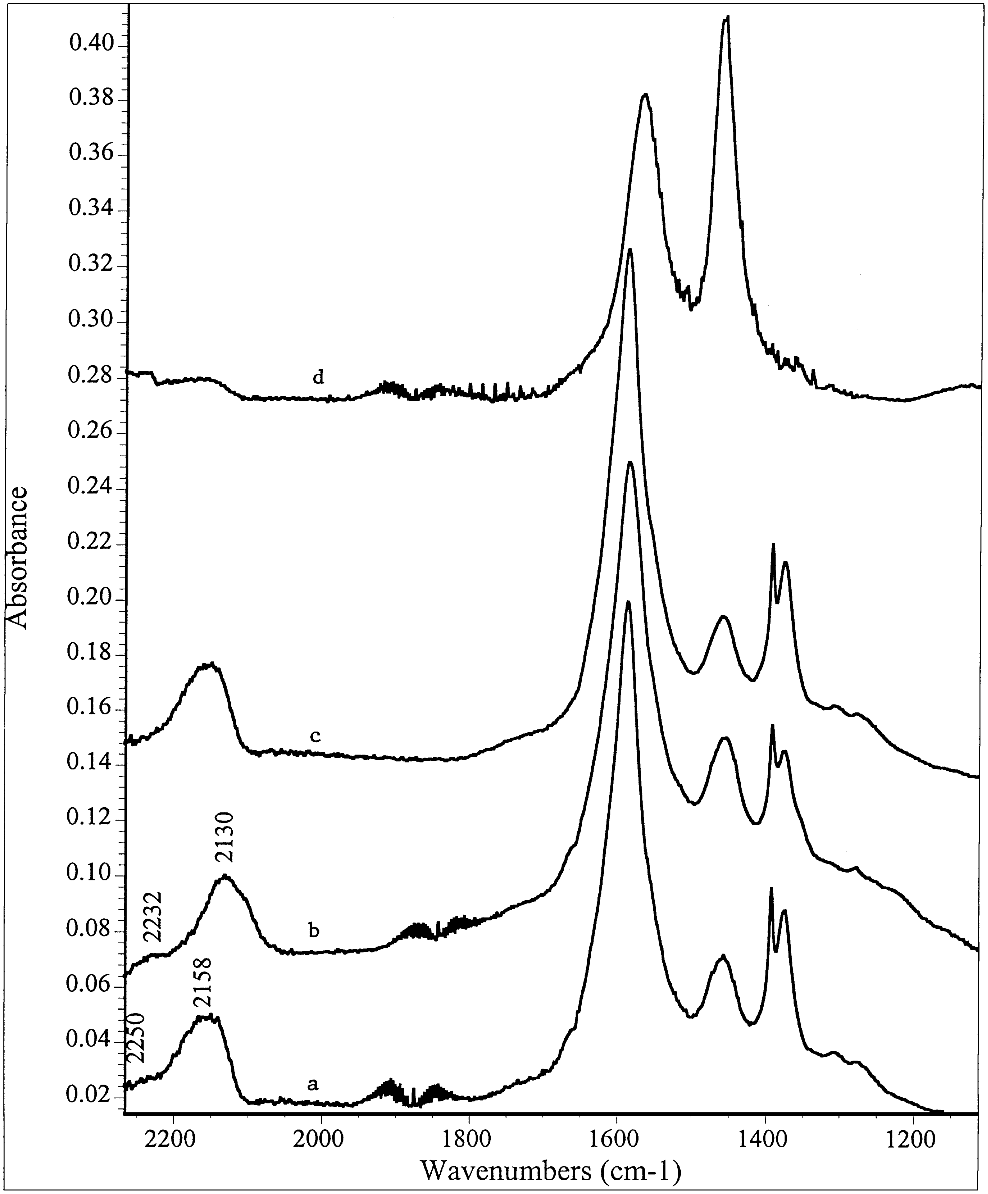

FIG. 6. *In situ* infrared spectra of an initially oxidized Pt/Al_2O_3 catalyst: (a) 2000 ppm NO, 2000 ppm C_3H_6, 2% O_2 in He for 55 min (250°C); (b) 2000 ppm ^{15}NO, 2000 ppm C_3H_6, 2% O_2 in He for 1 h (250°C); (c) flushing of (a) with He for 10 min (250°C); (d) 2000 ppm NO, 2000 ppm C_3H_6, 2% O_2 in He for 1 hr (350°C).

the isocyanate group because, under these conditions, the isocyanate peak is well resolved and is not interfered by the larger cyanide peak. The cell was then flushed with He (Fig. 8.1) for a period of 5 min. This resulted in a decrease in the intensity of the isocyanate peak to about half of its original value, indicating that, at 250°C, the isocyanate is weakly adsorbed. Flushing the cell with a 2% O_2/He mixture (Fig. 8.2) resulted in an almost complete disappearance of the isocyanate peak within the 5 min period, indicating that the isocyanate reacts with oxygen, in agreement with similar observations made recently with Pt/SiO_2 catalysts (36). The cell was also flushed for 5 min with NO/He, NO/O_2/He, and NO_2/He mixtures of variable NO_x concentrations. Flushing with 2000 ppm NO/He (Fig. 8.3) did not differ significantly from flushing with He, whereas, flushing with 2000 ppm NO/2% O_2/He or 2000 ppm NO_2/He (Fig. 8.4) resulted in spectra similar to the ones obtained during flushing with 2% O_2/He. However, when the NO_x concentration was increased to 1% (Figs. 8.5 and 8.6), the isocyanate peak completely disappeared within the 5 min period regardless of whether NO or NO_2 was flowed over the catalyst. These results show that the isocyanate species is reactive with the nitrogen oxides, a reaction which could lead to the formation of a N–N bond. Both NO and

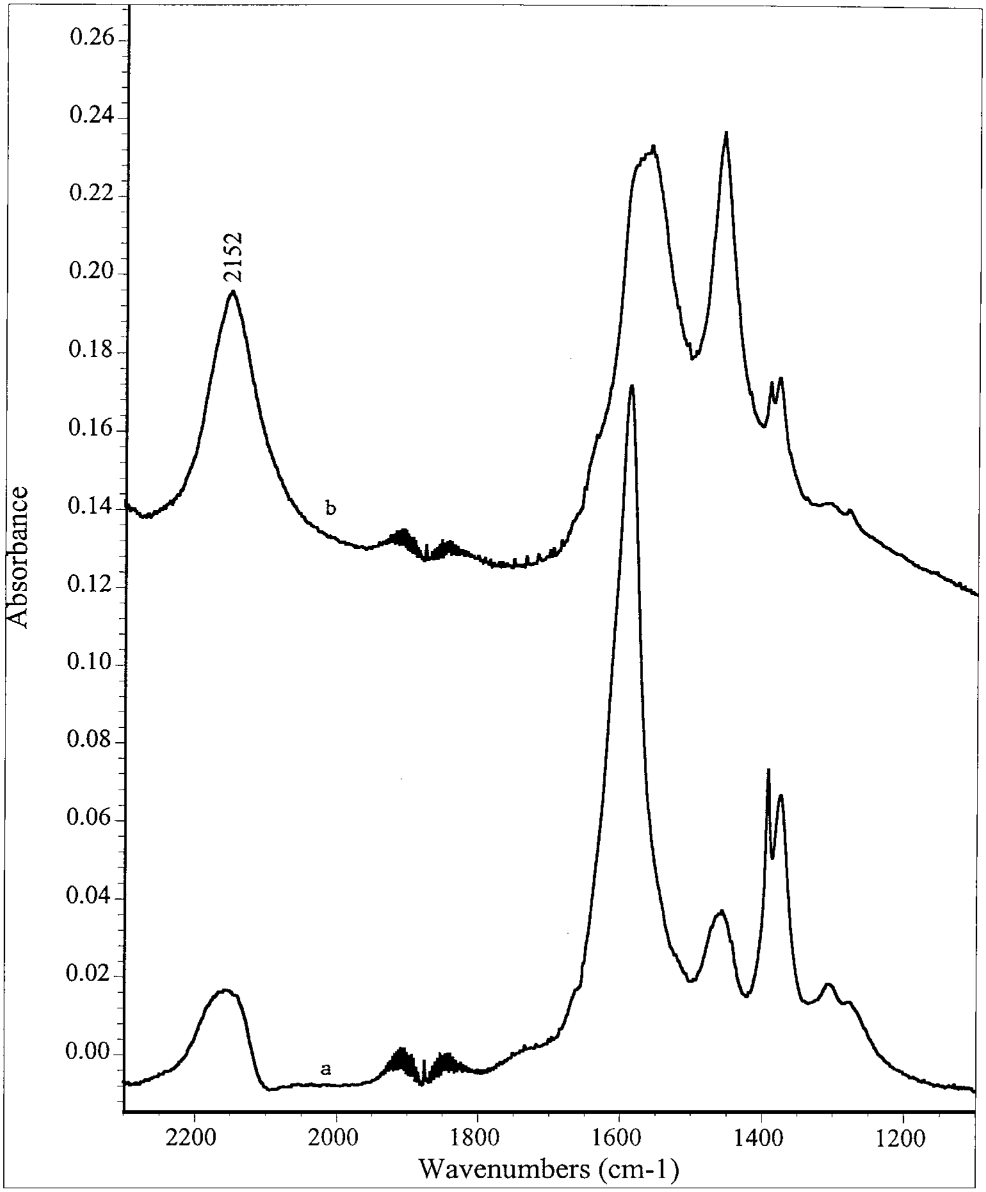

FIG. 7. *In situ* infrared spectra of an initially oxidized Pt/Al_2O_3 catalyst: (a) 2000 ppm NO, 2000 ppm C_3H_6 in He for 35 min (250°C); (b) 2000 ppm NO, 2000 ppm C_3H_6 in He for 30 min (350°C).

NO_2 react with the isocyanate group faster than oxygen at similar concentration levels (i.e., 1–2%). The rates of reaction are such, however, that under SCR conditions (i.e., high oxygen excess), the isocyanate group is only selective toward NO_2, which appears to be the nitrogen oxide that can effectively compete with O_2.

To further investigate the origin of the isocyanate species, studies were conducted with one reactant introduced to a surface exposed to the other. IR spectra collected during the flow of an $NO/O_2/He$ mixture over a Pt/Al_2O_3 catalyst pre-exposed to C_3H_6/O_2 are shown in Fig. 9. The first two spectra (Fig. 9a and 9b) are characteristic of a Pt/Al_2O_3 catalyst surface that has been exposed to a $C_3H_6/O_2/He$ mixture and flushed with He for approximately 10 min. After the sample has been exposed to the $NO/O_2/He$ mixture for 1 min (Fig. 9c), the isocyanate peak (2250 cm^{-1}) is noticed and then immediately disappears with time on stream (Fig. 9d), indicating that the $NO/O_2/He$ mixture reacts with surface species formed during adsorption of the hydrocarbon and forms the isocyanate. When the same experiment is conducted with the catalyst now being flushed with O_2 prior to exposure to the $NO/O_2/He$ mixture, no isocyanate formation is noticed, suggesting that in the absence of NO, the adsorbed species responsible

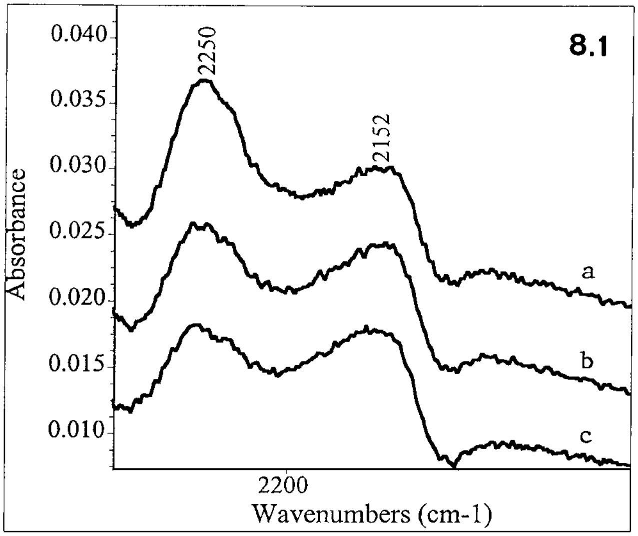

FIG. 8.1. *In situ* infrared spectra at 250°C of an initially oxidized Pt/Al_2O_3 catalyst: (a) 2000 ppm NO, 2000 ppm C_3H_6, 2% O_2 in He for 3 min; (b) flushing of (a) with He for 1 min; (c) flushing of (a) with He for 5 min.

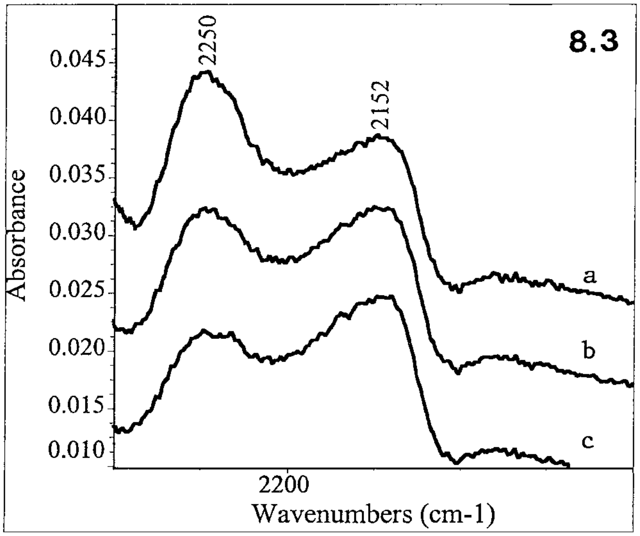

FIG. 8.3. *In situ* infrared spectra at 250°C of an initially oxidized Pt/Al_2O_3 catalyst: (a) 2000 ppm NO, 2000 ppm C_3H_6, 2% O_2 in He for 3 min; (b) flushing of (a) with 2000 ppm NO in He for 1 min; (c) flushing of (a) with 2000 ppm NO in He for 5 min.

for the formation of the isocyanate reacts with oxygen. When the above process was conducted in reverse order (i.e., $C_3H_6/O_2/He$ mixture flowed over a Pt/Al_2O_3 catalyst pre-exposed to NO), no formation of the isocyanate species was observed, suggesting that the isocyanate is a product of a reaction between an adsorbed hydrocarbon derivative and gas phase or weakly adsorbed NO/NO_x.

Finally, experiments were carried out in the presence of ca. 1% H_2O (Fig. 10a), since kinetic experiments suggest that the performance of Pt-based catalysts is not significantly affected by the presence of water (12, 16). The spectrum of Fig. 10a indicates that the cyanide and carboxylate groups were once again present, but there was no evidence of the isocyanate peak at 2250 cm^{-1}. This result prompted us to investigate the reactivity of the surface isocyanate species with water. Figure 10b is a spectrum of a Pt/Al_2O_3 catalyst exposed to a $NO/C_3H_6/O_2/He$ reacting mixture at 250°C for a period of 5 min. The cell was then flushed with a 0.5%

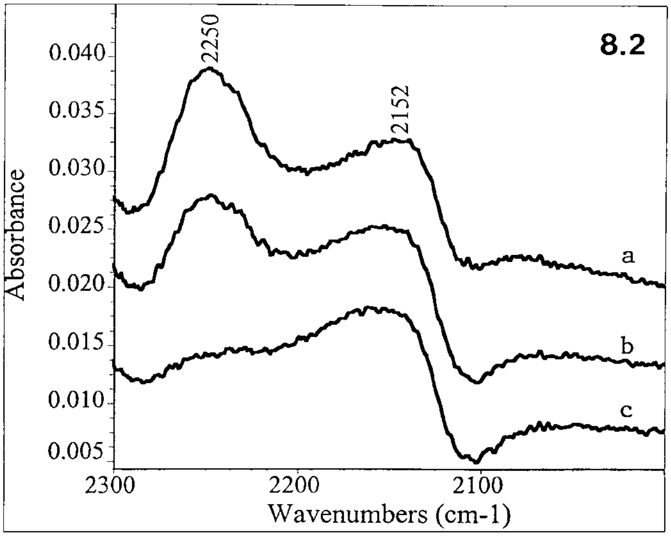

FIG. 8.2. *In situ* infrared spectra at 250°C of an initially oxidized Pt/Al_2O_3 catalyst: (a) 2000 ppm NO, 2000 ppm C_3H_6, 2% O_2 in He for 3 min; (b) flushing of (a) with 2% O_2 in He for 1 min; (c) flushing of (a) with 2% O_2 in He for 5 min.

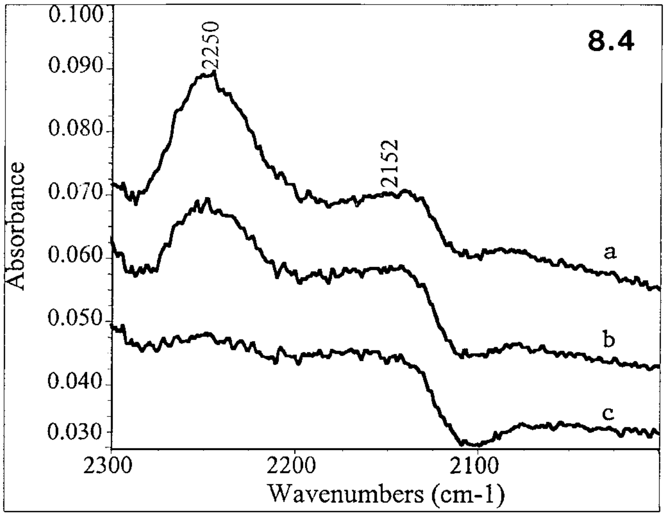

FIG. 8.4. *In situ* infrared spectra at 250°C of an initially oxidized Pt/Al_2O_3 catalyst: (a) 2000 ppm NO, 2000 ppm C_3H_6, 2% O_2 in He for 3 min; (b) flushing of (a) with 2000 ppm NO_2 in He for 1 min; (c) flushing of (a) with 2000 ppm NO_2 in He for 5 min.

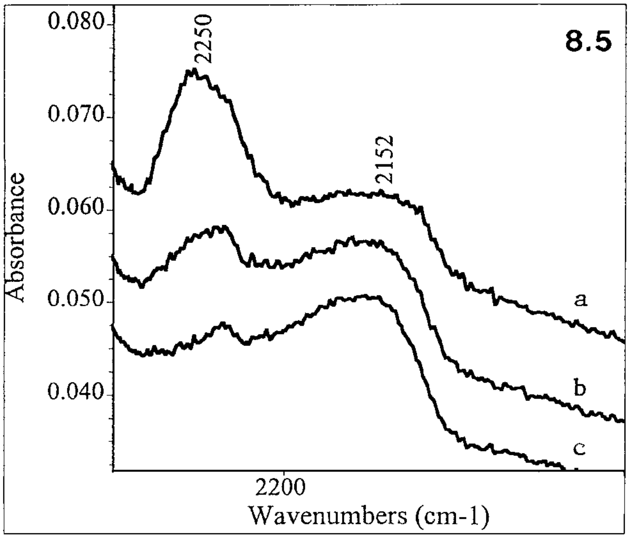

FIG. 8.5. *In situ* infrared spectra at 250°C of an initially oxidized Pt/Al_2O_3 catalyst: (a) 2000 ppm NO, 2000 ppm C_3H_6, 2% O_2 in He for 3 min; (b) flushing of (a) with 1% NO in He for 1 min; (c) flushing of (a) with 1% NO in He for 5 min.

H_2O/He mixture (Fig. 10c). Exposure of the sample to water resulted in a complete disappearance of the isocyanate peak within a 3-min period. This result is in agreement with recent SCR studies which also point out that surface isocyanates can hydrolyze under SCR conditions if water is present in the gas phase (37, 38). Ammonia, which is the product of this reaction, can selectively react with NO_x.

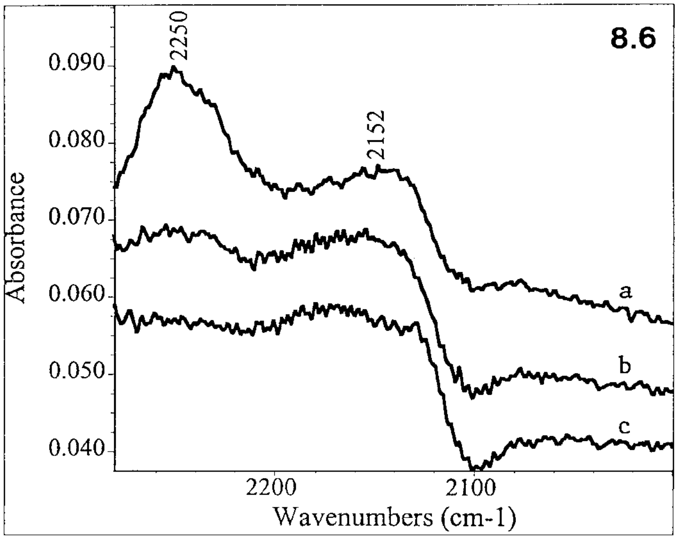

FIG. 8.6. *In situ* infrared spectra at 250°C of an initially oxidized Pt/Al_2O_3 catalyst: (a) 2000 ppm NO, 2000 ppm C_3H_6, 2% O_2 in He for 3 min; (b) flushing of (a) with 1% NO_2 in He for 1 min; (c) flushing of (a) with 1% NO_2 in He for 5 min.

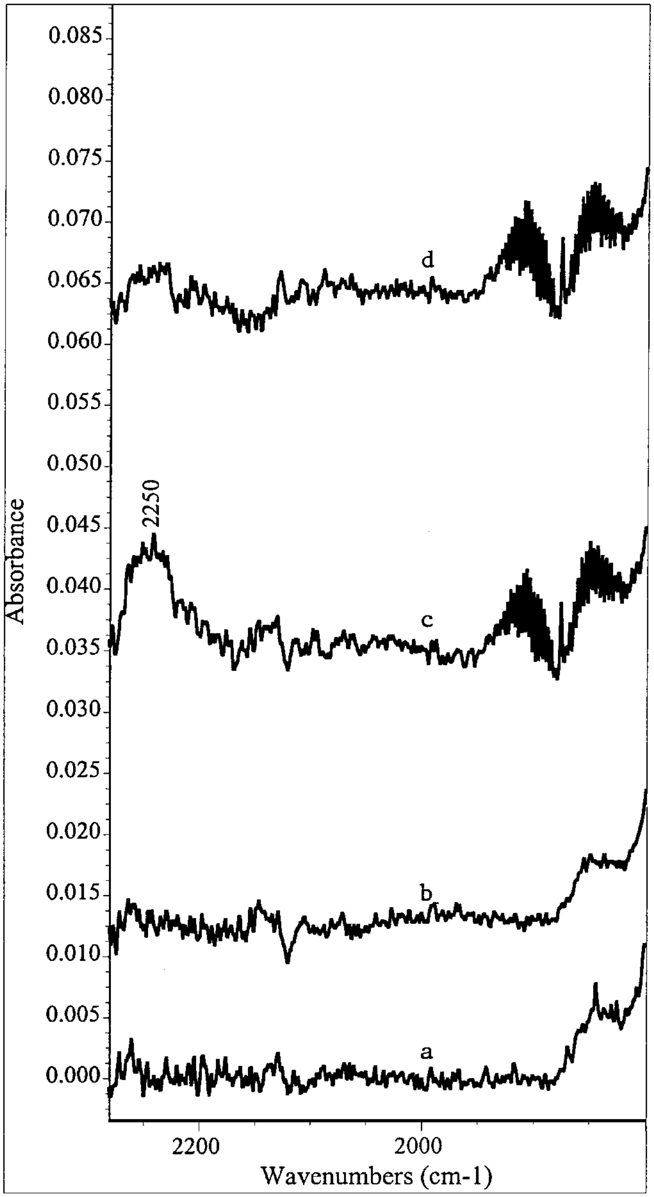

FIG. 9. *In situ* infrared spectra at 250°C of an initially oxidized Pt/Al_2O_3 catalyst: (a) 2000 ppm C_3H_6, 2% O_2 in He for 70 min; (b) flushing of (a) with He for 10 min; (c) flushing of (b) with 2000 ppm NO, 2% O_2 in He for 1 min; (d) flushing of (b) with 2000 ppm NO, 2% O_2 in He for 5 min.

CONCLUSION

Adsorption of NO on an oxidized Pt/Al_2O_3 catalyst results in the formation of surface NO^- species associated with Pt, as well as surface nitrates associated with the Al_2O_3 support. Similarly, adsorption of C_3H_6 on the same surface results in the formation of a mixture of formates and acetates associated with Al_2O_3 and an adsorbed CO species associated with Pt. Both carboxylates and nitrates are stable under the conditions studied and are not believed to participate in the HC–SCR reaction.

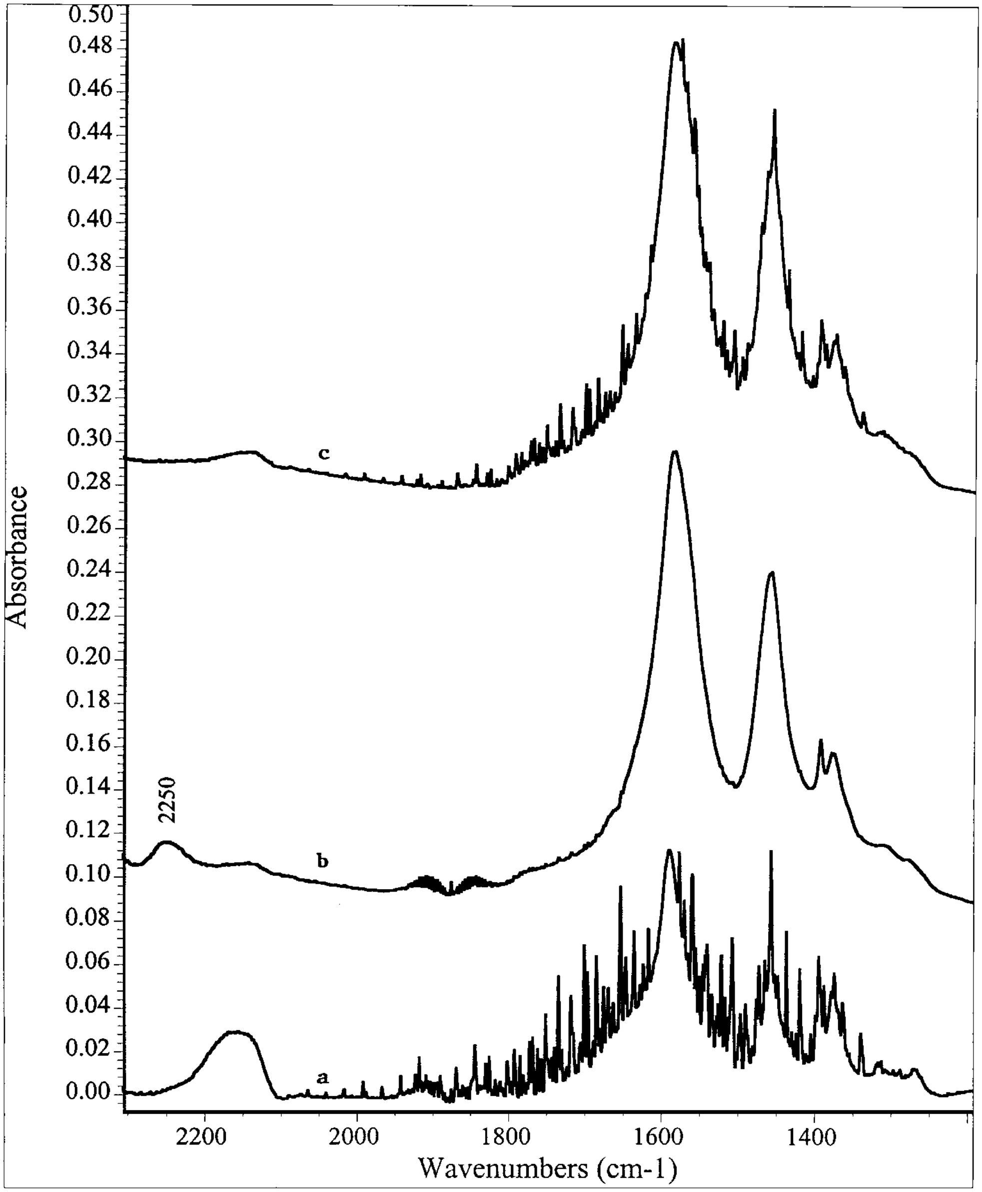

FIG. 10. *In situ* infrared spectra at 250°C of an initially oxidized Pt/Al_2O_3 catalyst: (a) 2000 ppm NO, 2000 ppm C_3H_6, 2% O_2, 1% H_2O in He for 1 h; (b) 2000 ppm NO, 2000 ppm C_3H_6, 2% O_2 in He for 5 min; (c) flushing of (b) with 0.5% H_2O in He for 3 min.

Under reaction conditions the formation of two additional species with characteristic IR peaks in the 2000–2300 cm^{-1} region are observed. These are believed to be surface cyanide (strong IR peak at 2158 cm^{-1}) and isocyanate species (shoulder at 2250 cm^{-1}). Reaction between NO and C_3H_6 in the absence of O_2 also produced the cyanide, but not the isocyanate species. The isocyanate species was intermittently observed when gas phase NO was flowed over a sample pre-exposed to propylene. Reaction between gas phase C_3H_6 and the surface species generated by the adsorption of NO on the catalyst did not result in the formation of either the cyanide or isocyanate group.

The cyanide and isocyanate species have been proposed in the past as reactive intermediates for the reduction of NO either by hydrocarbons (24, 39–41) or CO (33–35) over various catalysts. Their presence in our studies under reaction conditions poses the question of whether one, or both of them, may be such an intermediate for the selective reduction of NO by propylene over the Pt catalyst studied. We can confidently exclude the surface cyanide as such an intermediate. The formation of this species was observed even under conditions of very low SCR activity (i.e., in the absence of O_2); it is very strongly adsorbed on the catalyst surface and is not reacting in O_2, NO, NO_2, and NO/O_2

environments. On the contrary, the surface isocyanate species could be a potential reaction intermediate. This species is present only under SCR conditions (i.e., it is not present in the absence of O_2), is held weakly on the catalyst surface, and is reacting with O_2, NO, and NO_2. Its reaction is significantly faster with NO_2, indicating a strong selectivity toward this species. In the presence of water, the isocyanate is readily hydrolyzed, but the produced ammonia can selectively react with NO_x. Hence, both in the absence and in the presence of water, the isocyanate species can provide a pathway for the selective reduction of NO_x. Whether this is the main pathway or not still remains unclear.

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