

NO Reduction by Propylene over Pt/SiO₂: An *in Situ* FTIR Study

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The selective catalytic reduction (SCR) of nitric oxide (NO) by propylene (C₃H₆) over a 1 wt.% Pt/SiO₂ catalyst was studied by the use of *in situ* Fourier transform infrared (FTIR) spectroscopy at 250°C. At this temperature, introduction of NO to the catalyst did not result in the formation of any significant amounts of adsorbed NO_x-type species on either the catalyst or the SiO₂ support. On the contrary, introduction of C₃H₆ to the same catalyst resulted in the formation of surface carboxylates. Experiments conducted under reaction conditions resulted in the formation of a surface cyanide (–CN) species, and a gas phase/weakly adsorbed nitrous oxide (N₂O) species. The surface cyanide is the product of the reaction between an oxygen-activated hydrocarbon derivative and NO and is reactive toward NO, NO₂, and O₂, resulting in the formation of N₂ and N₂O. Its behavior, as observed in this study, is consistent with a role as a potential intermediate in the selective reduction of NO by propylene over the Pt/SiO₂ catalyst. © 2000

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INTRODUCTION

NO_x emissions are regulated by a variety of stringent laws at both the federal and local levels. Current commercial catalytic technologies for the control of NO_x emissions include the nonselective reduction by carbon monoxide and hydrocarbons over noble metal-based “three-way” catalysts, and the selective reduction by ammonia over vanadia/titania-based catalysts. Since its introduction in 1991 (1, 2), the selective reduction of NO by hydrocarbons has attracted a lot of interest, because it has certain advantages over both current technologies (3).

Supported platinum catalysts have shown significant activity toward the selective catalytic reduction of NO by hydrocarbons at low temperatures (3–10), and they are not significantly affected by the presence of water in the exhaust stream (1, 3, 7, 11, 12). Their drawbacks include a significant selectivity toward nitrous oxide (N₂O) and a narrow temperature window of operation (3–10, 13).

A number of studies have focused on the performance of Pt-based catalysts (2–18). However, the fundamental sur-

face chemistry involved in this reaction is still not clearly understood and is highly debated. This study aims toward the further development of such an understanding and complements our earlier work in this area (4, 5, 19). *In situ* FTIR studies were conducted with a Pt/SiO₂ catalyst at 250°C. Our previous kinetic studies indicate that at this temperature the catalyst is active but has not yet reached its maximum activity (5). Spectra were collected at atmospheric pressure over both the Pt/SiO₂ catalyst and the SiO₂ support under a variety of gas compositions. Studies with isotropically labeled nitric oxide (¹⁵NO) were also conducted to further qualify the identification of the surface species detected.

EXPERIMENTAL

Catalyst Preparation

The Pt/SiO₂ catalyst was prepared by incipient wetness impregnation of the SiO₂ support (Davison Syloid 74) with an aqueous solution of H₂PtCl₆·6H₂O (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 280 m²/g and a Pt loading of approximately 0.9 wt% (ICP-Galbraith Laboratories). Hydrogen chemisorption measurements indicate a Pt dispersion of approximately 60%.

Infrared Spectroscopy

Infrared spectra were collected with a Nicolet 740 FT-IR 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 samples and the corresponding references 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 elevated temperatures. The temperature was monitored through a thermocouple located in the cell in close proximity with the catalyst sample.

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Catalyst samples were prepared as self-supported wafers, 12 mm in diameter and with a "thickness" of about 20 mg/cm². Prior to each experiment the samples were pretreated at 250°C in a flowing 2% O₂ in He mixture for 2 h. Certified analyzed mixtures of 1.0% NO in He (Matheson), 1.0% NO₂ in He (Matheson), 1.0% C₃H₆ in He (National Specialty Gases), 10.0% O₂ in He (National Specialty Gases), 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/NO₂ and C₃H₆, and 2.0% of O₂. 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 cm³/min (1 atm, 25°C).

Reactor Studies

Transient reactor studies were conducted in a quartz, single-pass, fixed-bed, flow reactor. The volumetric flow rate of the reacting mixture was held at 100 cm³/min (1 atm, 25°C). Inlet and outlet gas mixtures were analyzed using a

gas chromatograph (Hewlett-Packard 5890) equipped with a thermal conductivity detector and a three-column system (Molecular Sieve 5A, Porapak Q, and Graphpac GC) for analysis of N₂, N₂O, CO, CO₂, and C₃H₆. Calibration curves were obtained for each of these species and the reproducibility of the measurements in each case was within ±5%. A thermocouple placed in the catalyst bed was used to monitor the temperature of the catalyst. Each run utilized approximately 500 mg of the Pt/SiO₂ catalyst in the form of 60/85 mesh particles.

RESULTS AND DISCUSSION

NO Adsorption

Pt/SiO₂. The spectrum of the Pt/SiO₂ catalyst following exposure to a mixture of 2000 ppm NO in He at 250°C for 45 min is shown in Fig. 1a. The gas phase NO doublet (centered at 1875 cm⁻¹) is the only feature in this spectrum, indicating the absence of any significant amounts of adsorbed species either on Pt or the silica support. This is consistent with previous literature reports indicating that adsorption of N_xO_y-type species on silica is only observed

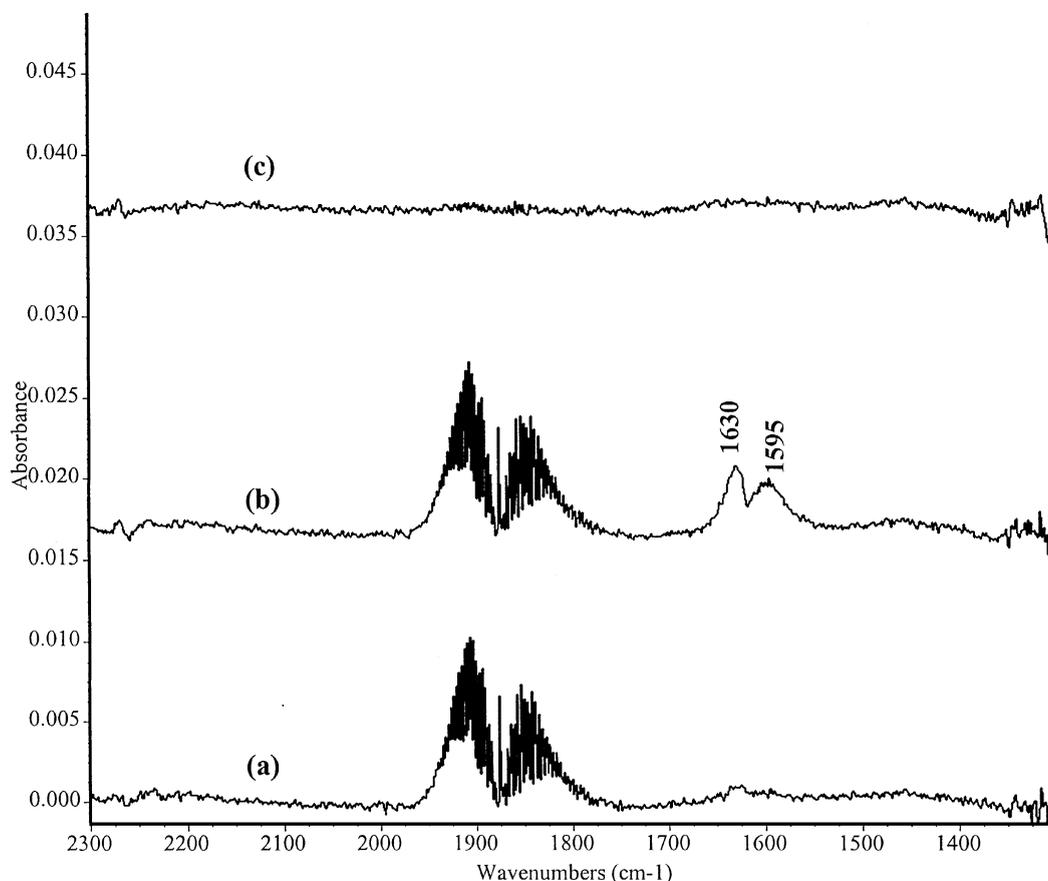


FIG. 1. *In situ* infrared spectra at 250°C of an initially oxidized Pt/SiO₂ catalyst: (a) 2000 ppm NO in He for 45 min; (b) 2000 ppm NO, 2% O₂ in He for 20 min; (c) flushing of (b) with He for 2 min.

at lower temperatures (20, 21). When 2% O₂ was added to the flowing NO mixture, a new doublet was observed at 1630 and 1595 cm⁻¹ (Fig. 1b). These two peaks correspond to the asymmetric stretching vibrations of NO₂ (22–24). However, when the sample was flushed with He (Fig. 1c), these two peaks disappeared immediately from the spectrum, indicating that the corresponding NO₂ species was either very weakly adsorbed or in the gas phase.

C₃H₆ Adsorption

SiO₂. The only peaks present in the spectrum of the silica support exposed to a mixture of 2000 ppm C₃H₆ in He at 250°C are those corresponding to gas phase propylene. Flushing the cell with He resulted in an immediate disappearance of these peaks, confirming that the observed propylene is either in the gas phase, or at most, very weakly adsorbed on the silica support.

Pt/SiO₂. The spectrum of the Pt/SiO₂ catalyst collected at 250°C following exposure to propylene (Fig. 2a), is significantly different from that of the SiO₂ support. This time, in addition to the gas phase peaks, a very broad peak centered at approximately 1550 cm⁻¹ is observed. Flushing the cell with He for 2 min (Fig. 2b), removes the gas phase propylene and resolves the broad peak into two peaks

centered at approximately 1530 and 1430 cm⁻¹. Similar peaks at approximately 1550 and 1440 cm⁻¹ have been previously observed during propylene oxidation over various metal oxides and have been assigned to surface carboxylate species, and more specifically, the asymmetric and symmetric -COO⁻ stretching vibrations (19, 25–30). These results indicate that during exposure of the oxidized Pt/SiO₂ catalyst to propylene at 250°C partial oxidation products are formed. The necessary oxygen for these reactions is present on the catalyst surface as a result of the catalyst oxidation pretreatment. Both peaks did not increase in intensity during our experiments after the first 6 min on stream, indicating that the surface oxygen needed for their formation had been depleted at that point. The intensities of both peaks corresponding to the surface carboxylate species decreased with increased time of flushing in He (Fig. 2c), indicating that either some type of surface rearrangement resulting in decreasing absorption cross section takes place, or that these species desorb from the surface under these conditions. In all probability conversion to the acid form takes place before desorption occurs. The cell was also flushed with 2% O₂/He and 2000 ppm NO/He mixtures in order to determine if the surface carboxylates are reactive toward these gases. The observed decrease in intensity in these cases was similar to when the cell was

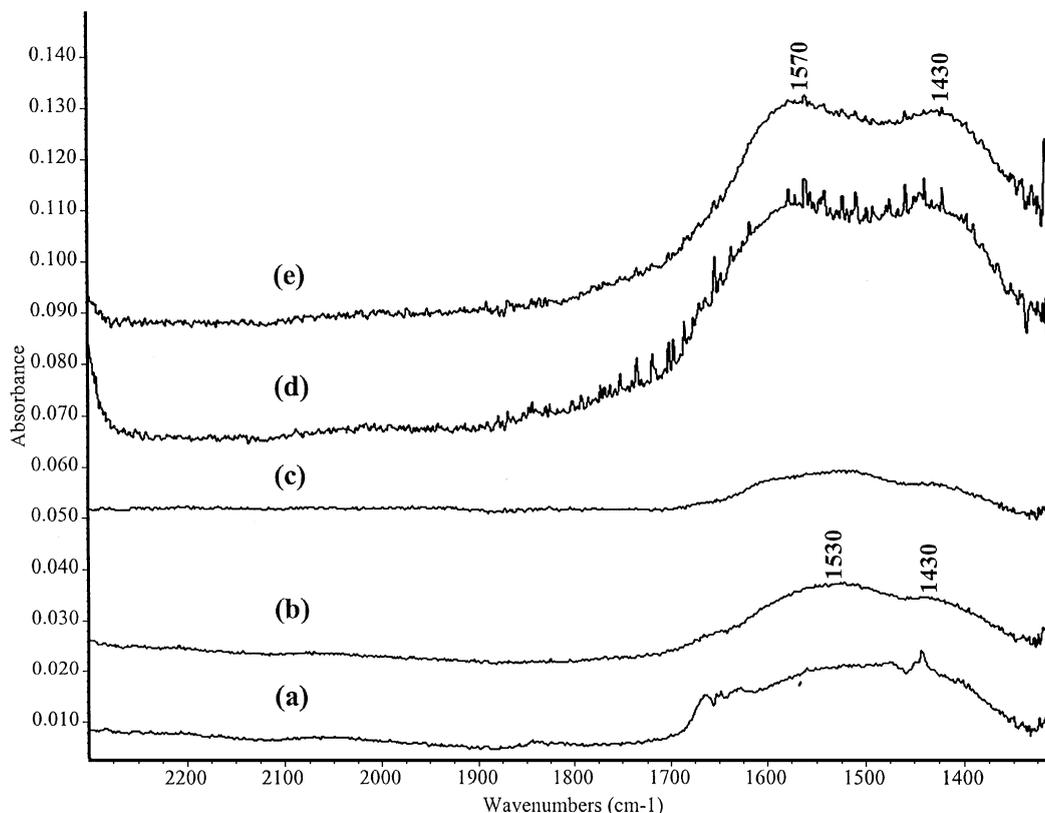


FIG. 2. *In situ* infrared spectra at 250°C of an initially oxidized Pt/SiO₂ catalyst: (a) 2000 ppm C₃H₆ in He for 30 min; (b) flushing of (a) with He for 2 min; (c) flushing of (a) with He for 20 min; (d) 2000 ppm C₃H₆, 2% O₂ in He for 30 min; (e) flushing of (d) with He for 2 min.

flushed with only He, indicating that the surface carboxylates are not reactive in O₂/NO environments under these conditions.

When 2% O₂ was added to the propylene stream (Fig. 2d), an increase in intensity of the IR peaks, and hence, the surface concentration of the carboxylate species was observed. Removal of the gas phase and flushing of the cell with He (Fig. 2e) reveals that the carboxylate peaks are broader and more intense in this case, with the peak at 1530 cm⁻¹ being shifted to approximately 1570 cm⁻¹.

Reaction Studies

The FTIR spectrum collected during the exposure of the Pt/SiO₂ catalyst to a mixture of 2000 ppm NO, 2000 ppm C₃H₆, and 2% O₂ in He at 250°C is shown in Fig. 3a. In addition to the peaks corresponding to gas phase NO and propylene and the adsorbed carboxylates, this spectrum also contains three new peaks at 2236, 2204, and 2090 cm⁻¹. When isotopically labeled nitric oxide (¹⁵NO) was used (Fig. 3b), the peak at 2090 cm⁻¹ shifts by 30 cm⁻¹ to 2060 cm⁻¹ indicating the presence of nitrogen in the corresponding species. Previous literature reports focusing on the adsorption of HCN on silica (31), have assigned a similar FTIR peak

at 2100 cm⁻¹, with a calculated $\Delta^{15}\text{N}$ shift of 28 cm⁻¹, to an adsorbed cyanide (-CN) species. Additionally, previous studies on HCN adsorption over a polycrystalline Pt foil also assigned a similar peak at 2086 cm⁻¹ to an adsorbed cyanide species (32). Consequently, we can also assign the observed peak at 2090 cm⁻¹ to an adsorbed cyanide species. Whether this species is on Pt or on the SiO₂ support is unclear, given the proximity of the cyanide assignments in the aforementioned previous studies. Upon removal of the reacting gas mixture and flushing of the cell with He (Fig. 3c) the peak at 2090 cm⁻¹ quickly disappears from the spectrum, indicating that the -CN species is weakly adsorbed on the surface.

The remaining two peaks in Fig. 3a, at 2236 and 2204 cm⁻¹, can be assigned to nitrous oxide (23, 24, 33). Their isotopic shifts to 2140 and 2170 cm⁻¹, respectively, are consistent with the proposed assignment, which was further confirmed by the introduction of gas phase N₂O to the Pt/SiO₂ catalyst. Kinetic results have shown that this catalyst is active under the conditions of the FTIR experiments and that N₂O is produced in significant amounts (5). Once again upon removal of the reacting gas mixture and flushing of the cell with He for 4 min (Fig. 3c), the two peaks corresponding to nitrous oxide disappear from the

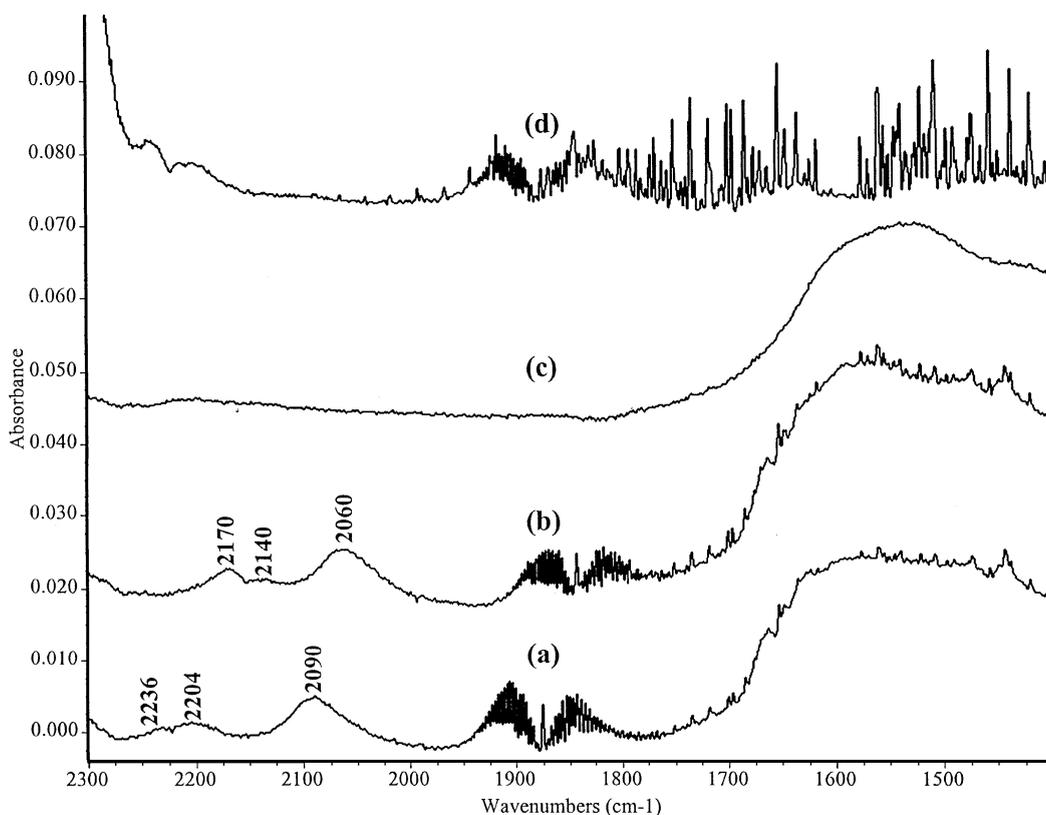


FIG. 3. *In situ* infrared spectra of an initially oxidized Pt/SiO₂ catalyst: (a) 2000 ppm NO, 2000 ppm C₃H₆, 2% O₂ in He for 1 h (250°C); (b) 2000 ppm ¹⁵NO, 2000 ppm C₃H₆, 2% O₂ in He for 1 h (250°C); (c) flushing of (a) with He for 4 min (250°C); (d) 2000 ppm NO, 2000 ppm C₃H₆, 2% O₂ in He for 40 min (350°C).

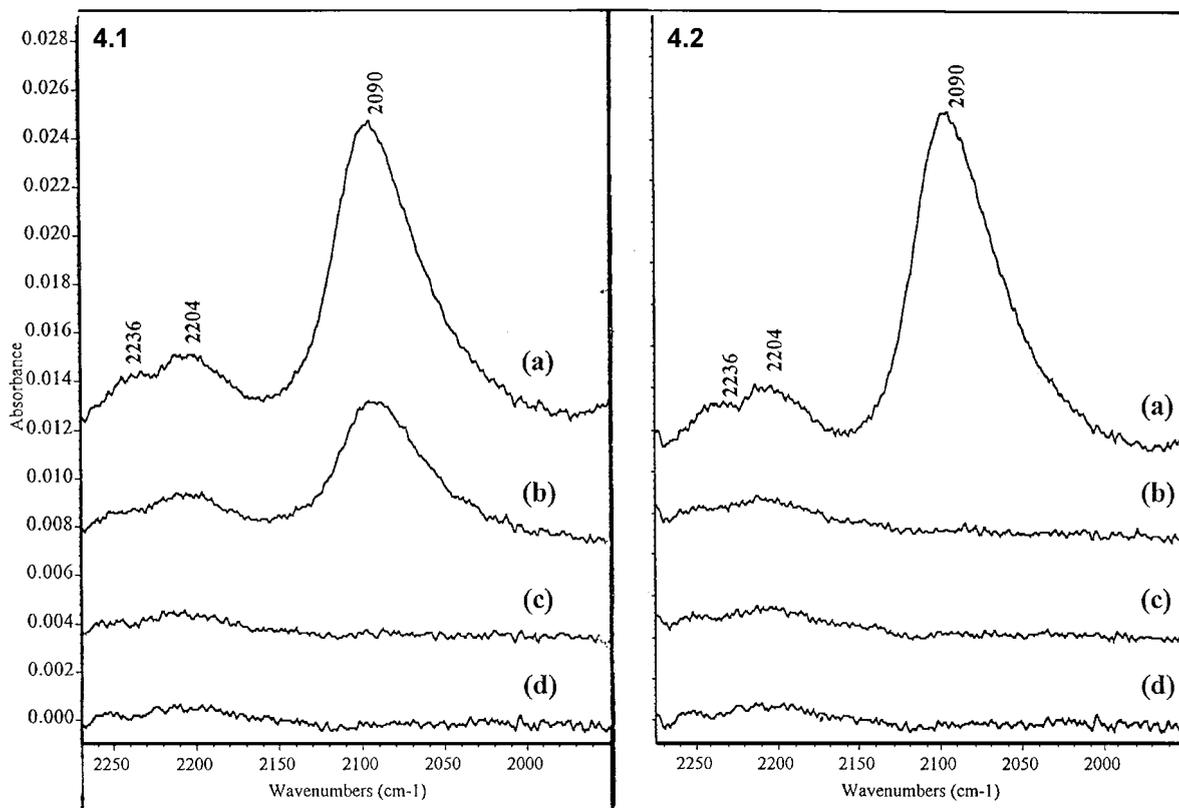


FIG. 4.1. *In situ* infrared spectra at 250°C of an initially oxidized Pt/SiO₂ catalyst: (a) 2000 ppm NO, 2000 ppm C₃H₆, 2% O₂ in He for 4 min; (b) flushing of (a) with He for 2 min; (c) flushing of (a) with He for 4 min; (d) flushing of (a) with He for 6 min. **(4.2)** *In situ* infrared spectra at 250°C of an initially oxidized Pt/SiO₂ catalyst: (a) 2000 ppm NO, 2000 ppm C₃H₆, 2% O₂ in He for 4 min; (b) flushing of (a) with 2% O₂ in He for 2 min; (c) flushing of (a) with 2% O₂ in He for 4 min; (d) flushing of (a) with 2% O₂ in He for 6 min.

spectrum indicating that the N₂O species responsible for them is either weakly adsorbed or in the gas phase.

The spectrum of the Pt/SiO₂ catalyst under reaction conditions at 350°C is shown in Fig. 3d. Our kinetic experiments (5) have shown that this temperature is above the temperature of maximum NO reduction, and propylene oxidation is reaching 100% under these conditions. In comparison to the spectrum collected at 250°C, several differences can be observed. The carboxylate peaks in the 1300–1700 cm⁻¹ region are no longer present, consistent with the complete oxidation of propylene. In addition, significant amounts of gas phase CO₂ and H₂O (the products of C₃H₆ oxidation) are observed, as evidenced by the strong peaks in the 2360–2320 cm⁻¹ and 1800–1400 cm⁻¹ regions, respectively. Finally, while the peak corresponding to adsorbed cyanide at 2090 cm⁻¹ is no longer present, the N₂O peaks at 2236 and 2204 cm⁻¹ are still visible.

Reactivity and Origin of the Cyanide Species

To further investigate the reactivity of the surface cyanide species observed, experiments were conducted with the SCR reactants being flowed over surfaces containing this

species. Spectra of the Pt/SiO₂ catalyst exposed to a mixture of NO/C₃H₆/O₂/He at 250°C for 4 min are shown as Figs. 4.1a through 4.5a. The catalyst was first flushed with He for a period of 6 min (Fig. 4.1). In this case, the intensity of the peak at 2090 cm⁻¹ decreased significantly after 2 min, and the peak completely disappeared after 4 min, consistent with the results shown in Fig. 3c. This indicates that the cyanide species is weakly adsorbed on the catalyst surface. During the same experiment, the N₂O doublet at 2236 and 2204 cm⁻¹ was also significantly lower in intensity after 2 min of He flushing and completely disappeared after 4 min, indicating that the observed N₂O species is either weakly adsorbed or in the gas phase.

Treating the catalyst sample with a 2% O₂ in He mixture (Fig. 4.2) resulted in a complete disappearance of the cyanide peak within the first two minutes of treatment, indicating the reaction of cyanide with oxygen. Surprisingly, treating the catalyst sample with a 2000 ppm NO in He mixture (Fig. 4.3) resulted in an apparent delay in the disappearance of the cyanide peak. In this case, the intensity of the cyanide peak was unchanged after 2 min of treatment, was reduced to half its original value after 4 min, and eventually disappeared only after 6 min. The N₂O doublet was

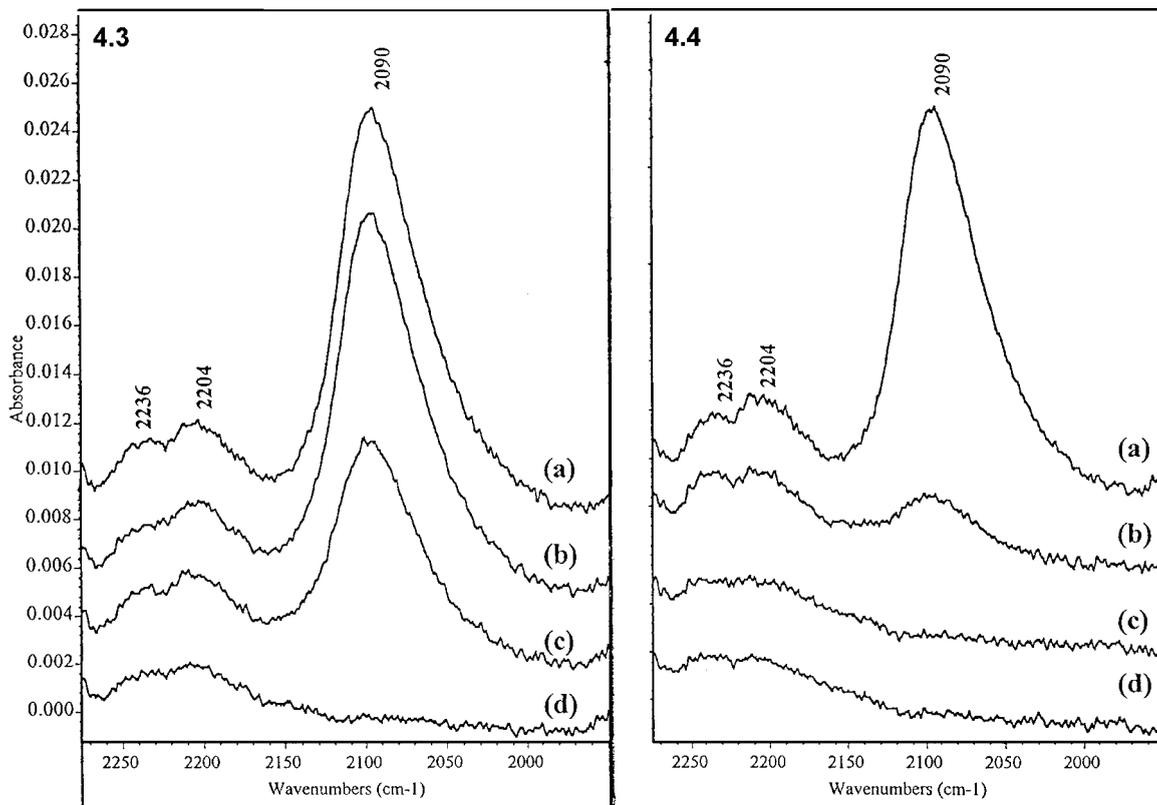


FIG. 4.3. *In situ* infrared spectra at 250°C of an initially oxidized Pt/SiO₂ catalyst: (a) 2000 ppm NO, 2000 ppm C₃H₆, 2% O₂ in He for 4 min; (b) flushing of (a) with 2000 ppm NO in He for 2 min; (c) flushing of (a) with 2000 ppm NO in He for 4 min; (d) flushing of (a) with 2000 ppm NO in He for 6 min. **(4.4)** *In situ* infrared spectra at 250°C of an initially oxidized Pt/SiO₂ catalyst: (a) 2000 ppm NO, 2000 ppm C₃H₆, 2% O₂ in He for 4 min; (b) flushing of (a) with 2000 ppm NO₂ in He for 2 min; (c) flushing of (a) with 2000 ppm NO₂ in He for 4 min; (d) flushing of (a) with 2000 ppm NO₂ in He for 6 min.

also present throughout the first six minutes, and in fact, did not completely disappear even after 6 min. In contrast, treatment of the catalyst sample with a 2000 ppm NO₂ in He mixture (Fig. 4.4) yielded results similar to those observed during the treatment with the O₂/He mixture (Fig. 4.2), in that the cyanide peak almost completely disappeared after 2 min of treatment, indicating that NO₂ reacts with this species at a rate comparable to that of O₂. N₂O appears to be one of the products of this reaction, since the intensity of the N₂O doublet after 2 min of treatment is higher in the case of NO₂ (Fig. 4.4b) than in the case of O₂ (Fig. 4.3b).

The unexpected nature of the results obtained during the treatment with the NO in He mixture prompted us to further investigate this case utilizing isotopically labeled ¹⁵N₂O. The results of this treatment are shown in Fig. 4.5. In this case, the cyanide peak is shifted to 2080 cm⁻¹ after 2 min and to 2060 cm⁻¹, the position corresponding to -C¹⁵N, after 4 min of treatment. At the same time, the N₂O doublet is shifted to 2140 and 2170 cm⁻¹ within the first two minutes of treatment and remains visible at this position even after 6 min. These results are consistent in terms of the overall intensities of the observed peaks with the results obtained with ¹⁴N₂O. The observed shifts in position, how-

ever, demonstrate that during the treatment with NO two parallel reactions that result in both the formation and consumption of the surface cyanide species take place. It is also clear that N₂O is a product of the CN-NO reaction, similar to the CN-NO₂ case. The above results are consistent with the findings of Bell *et al.* (34, 35) who reported that surface cyanide species adsorbed on Mn and Co-ZSM-5 catalysts are reactive in NO, O₂ and NO₂ environments.

The products of the reactions between the surface cyanide species and NO, O₂, and NO₂ were determined during transient reactor experiments conducted in parallel to the FTIR studies. The surface cyanide species was formed in this case by passing a mixture of 2000 ppm NO/2000 ppm C₃H₆/1% O₂/He through a fixed-bed reactor containing the Pt/SiO₂ sample, at a rate of 12,000 ml h⁻¹ g⁻¹. The NO/C₃H₆/O₂/He mixture was first flowed through the sample at 250°C for a period of 10 min. The reactor was subsequently flushed with He for a period of 2 min to purge the gas phase. This treatment was followed by a second pulse of either O₂, NO, NO₂, or He for 0.5 min. The IR results indicate that the adsorbed cyanide is still present on the catalyst surface following the 2-min He purge. When the sample was treated with He for a period of 2.5 min, a

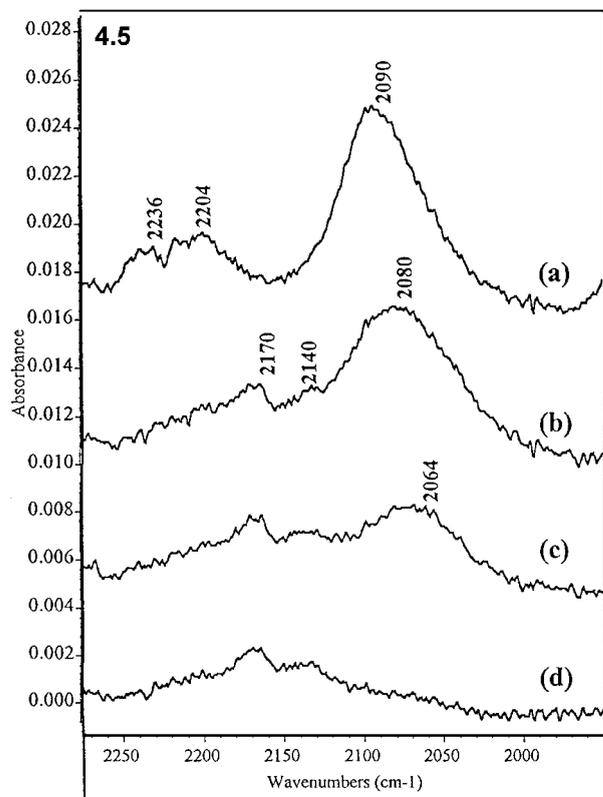


FIG. 4.5. *In situ* infrared spectra at 250°C of an initially oxidized Pt/SiO₂ catalyst: (a) 2000 ppm NO, 2000 ppm C₃H₆, 2% O₂ in He for 4 min; (b) flushing of (a) with 2000 ppm ¹⁵NO in He for 2 min; (c) flushing of (a) with 2000 ppm ¹⁵NO in He for 4 min; (d) flushing of (a) with 2000 ppm ¹⁵NO in He for 6 min.

significant decrease in the amount of N₂ (from 423 to 64 ppm) and N₂O (from 276 to 0 ppm) was observed in the exit stream (Table 1). Treatment of the sample with 2000 ppm O₂ (a concentration lower than the 1% was used

TABLE 1

Product Analysis during Transient Reactor Studies

Treatment	Exit stream concentrations		
	N ₂ (ppm)	CO ₂ (ppm)	N ₂ O (ppm)
NO/C ₃ H ₆ /O ₂ /He (10 min)	423	2411	276
NO/C ₃ H ₆ /O ₂ /He (10 min) He (2.5 min)	64	102	0
NO/C ₃ H ₆ /O ₂ /He (10 min) He (2 min)	161	355	14
O ₂ /He (0.5 min)			
NO/C ₃ H ₆ /O ₂ /He (10 min) He (2 min)	322	244	108
NO/He (0.5 min)			
NO/C ₃ H ₆ /O ₂ /He (10 min) He (2 min)	326	630	111
NO ₂ /He (0.5 min)			

in this case to facilitate on-line product analysis) for a period of 0.5 min following the 2-min He purge, resulted in the formation of N₂ (161 ppm) and a small amount of N₂O (14 ppm). Treatment of the sample with 2000 ppm NO for the same period also resulted in the formation of N₂ (322 ppm) and N₂O (108 ppm). The amounts of N₂ and N₂O however, are much greater in this case. Almost identical amounts of N₂ (326 ppm) and N₂O (111 ppm) were observed in the exit stream when the sample was treated with 2000 ppm NO₂. The above results indicate that N₂ and CO₂ are formed during the reaction of -CN and O₂, whereas N₂O is also formed during the reaction of -CN with NO and NO₂. Furthermore, the similar results obtained with NO and NO₂ show that the presence of NO₂ does not significantly enhance the CN-NO_x reaction.

To further investigate the origin of the cyanide species, studies were conducted with NO/He, NO₂/He, and NO/O₂/He mixtures being flowed over a surface that had been preexposed to C₃H₆/He or C₃H₆/O₂/He mixtures. The spectra collected during the flow of NO/He over a Pt/SiO₂ sample preexposed to C₃H₆ are shown in Fig. 5.1. Figure 5.1a is the spectrum of a surface exposed to a flow of C₃H₆ for 5 min and subsequently flushed with He for 2 min, in order to remove weakly adsorbed and gas phase propylene. NO was then flowed over this surface, and spectra were recorded at different time intervals as can be seen in Figs. 5.1b-5.1g. The results indicate that the flow of NO results in the formation of both the surface cyanide and the nitrous oxide product after a period of 4 min. Both species are present in very small amounts and remain on the surface even after 20 min of NO flow. The spectra of Fig. 5.1 demonstrate that the cyanide species can be formed by the reaction between an adsorbed hydrocarbon derivative and NO. When NO₂ was flowed over a similarly pretreated surface, no cyanide formation was observed, indicating that NO alone is responsible for this reaction.

Next, the same experiment was conducted, with oxygen being co-fed to the catalyst together with C₃H₆. In this case, when the catalyst was subsequently exposed to NO, the observed intensity of the surface cyanide peak at 2090 cm⁻¹ was significantly higher (Figs. 5.2b-5.2f). This result clearly demonstrates that the presence of O₂ during the adsorption of C₃H₆ eventually promotes the formation of the cyanide species, through what probably is an activation mechanism of the hydrocarbon. This result is consistent with our kinetic studies, which show that under similar conditions the rate of NO reduction by C₃H₆ is promoted by O₂ (5).

The same experiments were repeated with the catalyst treated with C₃H₆ in the absence of O₂, followed by a short (1 min) pulse of O₂. The cell was then once again flushed with He, and NO was subsequently introduced. The spectra collected in this case (Figs. 5.3b-5.3g) show a behavior similar to the one observed when O₂ was present during the treatment of the catalyst with C₃H₆ (Fig. 5.2). In both cases, there is a significantly higher amount of surface cyanide

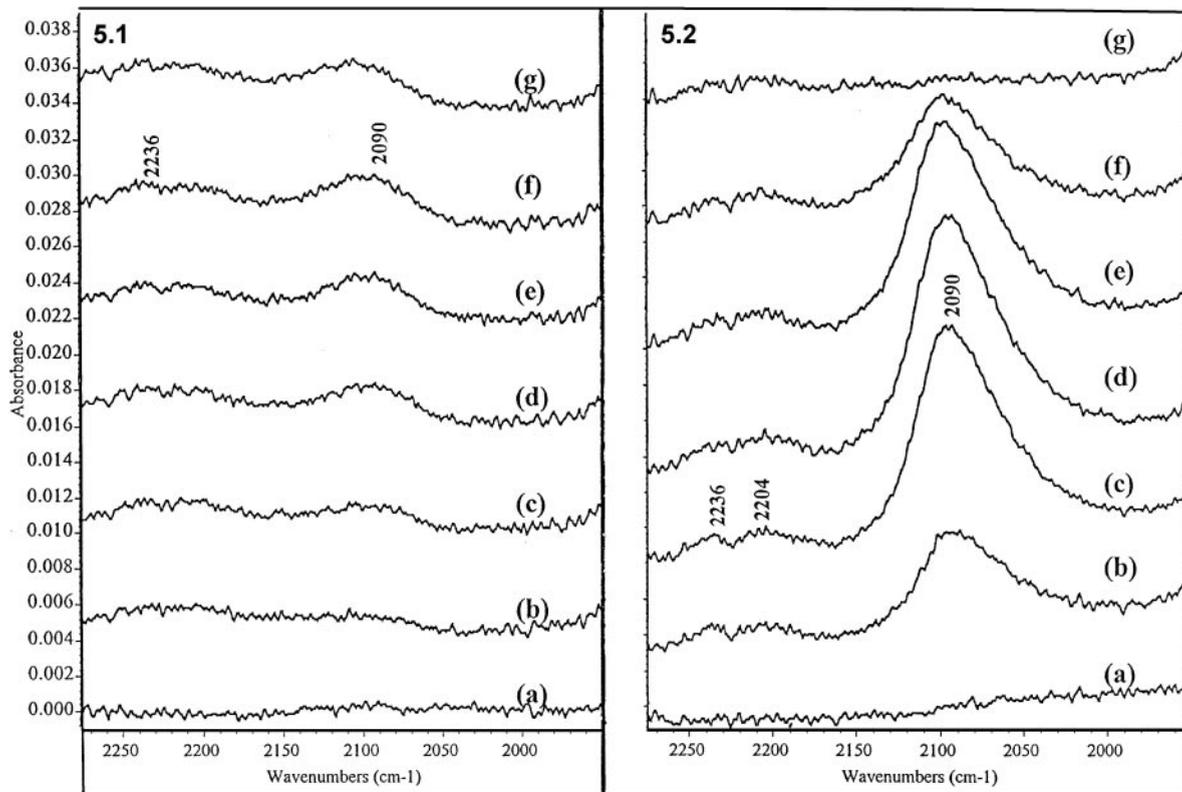


FIG. 5.1. *In situ* infrared spectra at 250°C of an initially oxidized Pt/SiO₂ catalyst, preexposed to 2000 ppm C₃H₆ in He for 5 min: (a) flushing with He for 2 min; followed by flushing with 2000 ppm NO in He for (b) 2, (c) 4, (d) 6, (e) 10, (f) 12, and (g) 20 min. **(5.2)** *In situ* infrared spectra at 250°C of an initially oxidized Pt/SiO₂ catalyst, preexposed to 2000 ppm C₃H₆, 2% O₂ in He for 5 min: (a) flushing with He for 2 min; followed by flushing with 2000 ppm NO in He for (b) 2, (c) 4, (d) 6, (e) 10, (f) 12, and (g) 20 min.

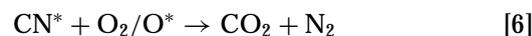
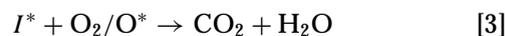
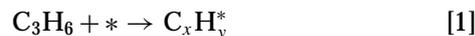
formed, indicating the promoting effect of O₂. The results of Fig. 5.3 further demonstrate that oxygen reacts with an adsorbed hydrocarbon species to form the activated species that eventually reacts with NO toward CN. It is important to note that when a longer pulse of oxygen was used (i.e., 5 min) no evidence was found in the IR spectra for the formation of either the surface cyanide or the nitrous oxide product. On the contrary, experiments with a prolonged He flushing of 5 min over a surface preexposed to C₃H₆, yielded results identical to those of Fig. 5.1, indicating that desorption of the active hydrocarbon species is not a problem. The results with the prolonged O₂ pulse suggest that oxygen can also react further and consume the activated hydrocarbon species, which is the precursor to -CN. These observations are once again consistent with the results of our kinetic studies (5), which demonstrated the dual role of oxygen in the reduction of NO: as an activating agent (at low concentrations) and as a competing oxidizing agent for the activated hydrocarbon (at higher concentrations).

Finally, the reduction of NO by propylene was conducted in the presence of approximately 1% H₂O at 250°C, and the spectrum collected at steady state is shown in Fig. 6b. The *in situ* spectra collected in the absence and presence of water are very similar with the exception of the presence of

rotational vibration peaks of gas phase H₂O (Fig. 6b). Our kinetic results indicate that the performance of the Pt/SiO₂ catalyst is not affected by the presence of H₂O, which is consistent with the spectra shown in Fig. 6.

Mechanistic Implications

Based on the results presented in this paper and our earlier kinetic studies (5), the following reaction pathway is proposed for the selective catalytic reduction of NO by propylene over Pt/SiO₂ at temperatures below the temperature of maximum NO conversion:



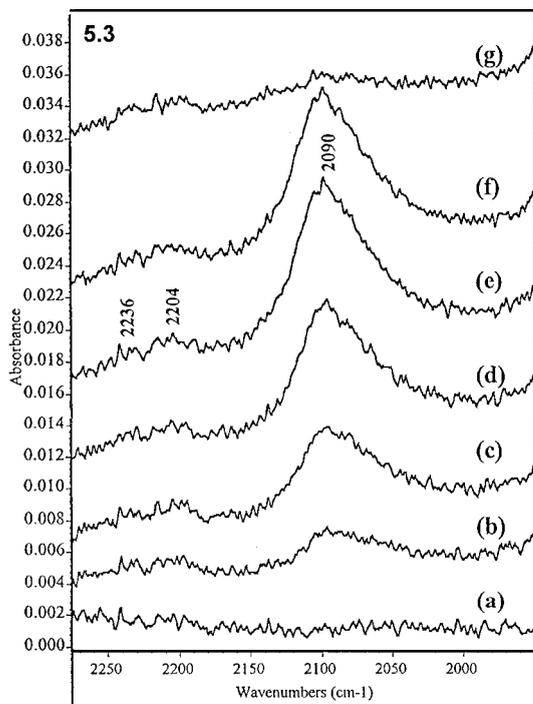


FIG. 5.3. *In situ* infrared spectra at 250°C of an initially oxidized Pt/SiO₂ catalyst, preexposed to 2000 ppm C₃H₆ in He for 5 min and subsequently flushed with 2% O₂ in He for 1 min: (a) flushing with He for 2 min, followed by flushing with 2000 ppm NO in He for (b) 2, (c) 4, (d) 6, (e) 10, (f) 12, and (g) 20 min.

The steps of this pathway are not intended to represent formal stoichiometrically balanced chemical reactions. Instead, they are simply indicating the origin and reactivity of the various species that are, in our opinion, involved in the reaction.

Step 1 indicates that an adsorbed hydrocarbon species is involved in the reaction, consistent with the results presented in Fig. 5. Steps 2 and 3 demonstrate the dual role of oxygen as an activating agent for propylene (step 2) and as a competing oxidizing agent (step 3) and are consistent with the results shown in Figs. 5.2 and 5.3 and the previous kinetic results. The exact nature of the activated hydrocarbon intermediate (I^*) is not currently known, although it is clear from the results of Figs. 5.2 and 5.3 that this species is adsorbed on the catalyst. Our experiments cannot differentiate and identify the form of oxygen involved in this, as well as subsequent steps (i.e., gas phase or adsorbed, molecular, or atomic), and hence the two general forms are shown in the proposed pathway. Step 4 suggests that the reaction toward the formation of an active intermediate, and eventually -CN, can also proceed in the absence of oxygen as indicated by the results of Fig. 5.1. The rate of this reaction and/or the subsequent reaction for the formation of -CN is significantly lower than the rate of step 2. Furthermore, it is not clear if the same activated intermediate is formed both in the presence and absence of oxygen. Step 5 represents the formation of the surface cyanide species. Evidence for this

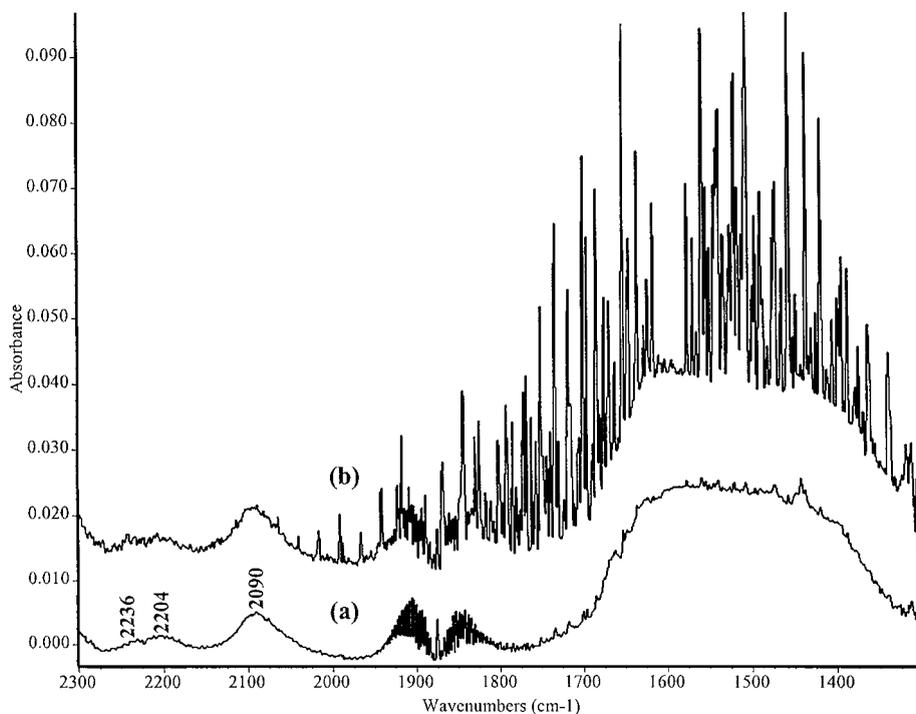


FIG. 6. *In situ* infrared spectra at 250°C of an initially oxidized Pt/SiO₂ catalyst: (a) 2000 ppm NO, 2000 ppm C₃H₆, 2% O₂ in He for 1 h; (b) 2000 ppm NO, 2000 ppm C₃H₆, 2% O₂, 1% H₂O in He for 1 h.

step is abundant in the spectra of Figs. 4.5 and 5.1–5.3. The exact form of the nitrogen oxide involved (i.e., gas phase or adsorbed) is debatable, although our kinetic and spectroscopic results appear to suggest that gas phase or weakly adsorbed nitric oxide (NO) is primarily involved. Step 6 represents the oxidation of the surface cyanide intermediate by oxygen. Evidence for this step is shown in Fig. 4.2. The products of this reaction, as shown in Table 1, are primarily N₂ and CO₂. Finally, step 7 represents the reaction of –CN with nitrogen oxides as evident from the results shown in Figs. 4.4 and 4.5. N₂, N₂O, and CO₂ are the products of this reaction (Table 1). The mechanisms of N₂ and N₂O formation are not currently understood clearly. One possible pathway includes the formation of surface atomic nitrogen (N), which can desorb as N₂ or combine with NO to form N₂O.

The proposed mechanism cannot answer every question about this reaction; in fact, it generates several questions as pointed out in the previous paragraph. It is not clear yet if this pathway is the only one in operation, for example. What is clear however, is that the proposed scheme is a major reaction pathway for the reduction of NO under the conditions of this study. Strong experimental evidence from both our kinetic and FTIR studies supports this statement.

CONCLUSIONS

Introduction of NO at 250°C to an oxidized Pt/SiO₂ sample did not result in the formation of any significant amounts of adsorbed NO_x-type species, associated with either the Pt catalyst or the silica support. On the contrary, the adsorption of C₃H₆ under the same conditions resulted in the formation of carboxylate species on the catalyst surface. Pt catalyzes the formation of these species, although it is possible, that following their formation they migrate to the silica support. The necessary oxygen for these reactions is present on the catalyst surface as a result of the oxidation pretreatment. As expected, when oxygen is co-fed with propylene, the intensity of all peaks associated with these partial oxidation products is significantly higher.

Under reaction conditions the formation of two new species is observed with characteristic IR peaks in the 2000–2300 cm⁻¹ region. These have been assigned to a surface cyanide (peak at 2090 cm⁻¹) and a gaseous/weakly adsorbed nitrous oxide (doublet at 2236 and 2204 cm⁻¹) species. Pt catalyzes the formation of both. Experiments conducted in an attempt to probe the origin of the surface cyanide species indicate that this species is formed as a result of the reaction between NO and a surface hydrocarbon derivative. Small amounts of oxygen assisted the activation of the adsorbed hydrocarbon and enhanced the formation of the surface cyanide.

The reactivity of the surface cyanide was also studied, and the results show that this species could be a potential

reaction intermediate in the reduction of NO by C₃H₆. This species is held relatively weakly on the catalyst surface and is reacting with O₂, NO, and NO₂. The formation of N₂, N₂O, and CO₂ was observed as a result of the CN–NO and CN–NO₂ reactions while N₂ and CO₂ are the products of the CN–O₂ reaction. Additionally, the surface concentration of the cyanide was not affected by the presence of water in the reacting gas mixture. The conclusions of these FTIR studies are in excellent agreement with our previous kinetic work with the same catalyst.

We have recently reported the results of similar FTIR studies of the same reaction over a Pt/Al₂O₃ catalyst with the same Pt content (19). In that case, and in agreement with other published reports (36–41), we concluded that a surface isocyanate species (–NCO) is a potential reaction intermediate. The presence of a surface cyanide species was also identified on the Pt/Al₂O₃ catalyst, but this species was very stable and did not react with either O₂ and/or NO_x. We have not been able to detect the formation of any surface isocyanates on the Pt/SiO₂ catalyst under the conditions studied. The isocyanate species is known to adsorb on SiO₂ with a characteristic IR peak at 2310 cm⁻¹ (31). Since this is in the region of the IR absorption of gas phase CO₂ (a product of the SCR reaction), it is possible that a weak peak in this region is covered in our spectra by the strong CO₂ doublet between 2360 and 2320 cm⁻¹.

A reaction mechanism was proposed for the selective catalytic reduction of NO by C₃H₆ over a Pt/SiO₂ catalyst. While it is conceivable that other pathways may also be in operation, experimental evidence from our infrared and kinetic work strongly supports the notion that the proposed scheme is a major route for the reduction of NO under the conditions studied.

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REFERENCES

1. Iwamoto, M., and Hamada, H., *Catal. Today* **10**, 57 (1991).
2. Held, W., Koenig, A., Richter, T., and Puppe, L., SAE Paper 900496.
3. Amiridis, M. D., Zhang, T., and Farrauto, R. J., *Appl. Catal. B* **10**, 203 (1996).
4. Roberts, K. L., and Amiridis, M. D., *Ind. Eng. Chem. Res.* **36**, 3529 (1997).
5. Captain, D. K., Roberts, K. L., and Amiridis, M. D., *Catal. Today* **42**, 93 (1998).
6. Sasaki, M., Hamada, H., Kintaichi, Y., Ito, Y., and Tabata, M., *Catal. Lett.* **15**, 297 (1992).
7. Hirabayashi, H., Yahiro, H., Mizuno, N., and Iwamoto, M., *Chem. Lett.* 2235 (1992).
8. Burch, R., and Millington, P. J., *Catal. Today* **29**, 37 (1996).
9. Burch, R., Millington, P. J., and Walker, A. P., *Appl. Catal. B* **4**, 65 (1994).
10. Burch, R., and Ottery, D., *Appl. Catal. B* **9**, L19 (1996).

11. Yahiro, H., Hirabayashi, H., Shin, H. K., Mizuno, N., and Iwamoto, M., *Trans. Mater. Res. Soc. Jpn. A* **18**, 409 (1994).
12. Efthimiadis, E. A., Lionta, G. D., Christoforou, S. C., and Vasalos, I. A., *Catal. Today* **40**, 15 (1998).
13. Hamada, H., Kintaichi Y., Sasaki, M., Ito, T., and Tabata, M., *Appl. Catal.* **75**, L1 (1991).
14. Tanaka, T., Yokota, K., Isomura, N., Doi, H., and Sugiura, M., *Appl. Catal. B* **16**, 199 (1998).
15. Bamwenda, G. R., Obuchi, A., Ogata, A., Oi, J., Kushiyama, S., and Mizuno, K., *J. Mol. Catal. A* **126**, 151 (1997).
16. Gulari, E., and Seker, E., *J. Catal.* **179**, 339 (1998).
17. Eckhoff, S., Hesse, D., van den Tillaart, J. A. A., Leyrer, J., and Lox, E. S., *Stud. Surf. Sci. Catal.* **116**, 223 (1998).
18. Monroe, D., DiMaggio, C. L., Beck, D. D., and Matekunas, F. A., SAE Paper 930737, 1993.
19. Captain, D. K., and Amiridis, M. D., *J. Catal.* **184**, 377 (1999).
20. Djonev, B., Tsyntsarski, B., Klissurski, D., and Hadjiivanov, K., *J. Chem. Soc. Faraday Trans.* **93**, 4055 (1997).
21. Ghiotti, F., Garrone, E., and Boccuzzi, F., *J. Phys. Chem.* **91**, 5640 (1987).
22. Wilson, M. K., and Badger, R. M., *Phys. Rev.* **76**, 472 (1949).
23. Nightingale, R. E., Downie, A. R., Rotenberg, D. L., Crawford, B., and Ogg, R. A., *J. Phys. Chem.* **61**, 1047 (1954).
24. Laane, J., and Ohlsen, J. R., *Prog. Inorg. Chem.* **27**, 465 (1980).
25. Gerei, S. V., Rozhkova, E. V., and Goraokhovatsky, Y. A. B., *J. Catal.* **28**, 341 (1973).
26. Long, R. Q., and Yang, R. T., *J. Phys. Chem. B* **103**, 2232 (1999).
27. Busca, G., *Catal. Today* **27**, 457 (1996).
28. Hoost, T. E., Laframboise, K. A., and Otto, K., *Catal. Lett.* **37**, 153 (1996).
29. Escribano, E. S., Busca, G., and Lorenzelli, V., *J. Phys. Chem.* **94**, 8939 (1990).
30. Finocchio, E., Busca, G., Lorenzelli, V., and Willey, R. J., *J. Catal.* **151**, 204 (1995).
31. Morrow, B. A., and Cody, I. A., *J. Chem. Soc. Faraday Trans. I* **71**, 1021 (1975).
32. Levoguer, C. L., and Nix, R. M., *J. Chem. Soc. Faraday Trans.* **92**, 4799 (1996).
33. Richardson, W. S., and Wilson, E. B., *J. Chem. Phys.* **18**, 694 (1950).
34. Aylor, A. W., Lobree, L. J., Reimer, J. A., and Bell, A. T., *J. Catal.* **170**, 390 (1997).
35. Lobree J. J., Aylor, A. W., Reimer, J. A., Bell, A. T., *J. Catal.* **169**, 188 (1997).
36. Bamwenda, G. R., Ogata, A., Obuchi, A., Oi, J., Mizuno, A., and Skrzypek, J., *Appl. Catal. B* **6**, 311 (1995).
37. Coronado, J. M., and Anderson, J. A., *J. Mol. Catal. A* **138**, 83 (1999).
38. Tanaka, T., Okuhara, T., and Misono, M., *Appl. Catal. B* **4**, L1 (1994).
39. Okuhara, T., Hasada, Y., and Misono, M., *Catal. Today* **35**, 83 (1997).
40. Obuchi, A., Wogerbauer, C., Koppel, R., and Baiker, A., *Appl. Catal. B* **19**, 9 (1998).
41. Haneda, M., Kintaichi, Y., Inaba, M., and Hamada, H., *Catal. Today* **42**, 127 (1998).