

An investigation of the role of surface nitrate species in the oxidation of propene on a Pt-based diesel oxidation catalyst†

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Enhancing the low temperature activity of diesel oxidation catalysts is important for cold-start conditions and the possible importance of nitrate species in oxidation reactions has been proposed although definitive evidence has not been reported. To investigate the possible role of surface nitrates, their adsorption and reactivity on a Pt-based diesel oxidation catalyst have been investigated using the Short Time on Stream (STOS) transient kinetic technique. The results provide for the first time definitive evidence for the oxidation of propene by some of these nitrate-type species.

1. Introduction

Diesel engine aftertreatment has received considerable attention over the last several years. Commercial systems include a diesel oxidation catalyst (DOC) upstream of a selective catalytic reduction (SCR) of NO_x catalyst and/or a NO_x storage/reduction (NSR) catalyst.^{1,2} The role of the DOC is to oxidize CO and hydrocarbon species exiting the combustion process, to oxidize NO to NO₂ and to periodically provide heat for the downstream components *via* exothermic hydrocarbon oxidation. The NO oxidation functionality is important for the NO_x reduction catalysts, as the SCR reaction rate is highest with an equimolar mixture of NO and NO₂, the so-called fast SCR reaction,^{3,4} and NSR catalysts trap NO₂ more readily than NO,^{5–9} thereby improving NO_x storage performance^{10–13} as the engine out ratios of NO:NO₂ are typically high. The formed NO₂ can also oxidize soot at significantly lower temperatures than O₂.¹ DOCs are typically comprised of Pt, Pd or Pt–Pd blends, due to their oxidation ability, supported on a high surface area oxide.^{14–21}

Recent evidence^{14,15} has pointed to the possibility that NO₂ is also involved in the oxidation of CO and hydrocarbons over the DOC. Under certain circumstances, NO₂ has been shown to

be preferentially consumed relative to O₂ in the oxidation reaction.^{14,15} This leads to no NO₂ observed until all, or most, of the CO and hydrocarbons are oxidized and it is only after they are combusted is NO₂ observed. Katare and co-workers²² also showed that as a DOC is thermally aged, this effect becomes more pronounced since the activity of the catalyst for the oxidation of CO and hydrocarbon drops. The definitive elucidation of the role of species such as surface nitrates for alumina-supported catalysts lies in the difficulty in differentiating between active and spectator surface species that build up during catalyst exposure to reactants.^{23–25} As an example, Chansai *et al.*²⁴ have observed nitrates species of different reactivities during H₂-enhanced hydrocarbon SCR of NO_x over Ag-based catalysts. Upon exposure to NO_x, a significant amount of nitrate species can form on Pt/Al₂O₃ catalysts, and as mentioned above, some of these surface nitrates may participate in hydrocarbon oxidation. To confirm the involvement of some types of surface nitrates, the Short Time on Stream (STOS) DRIFTS technique^{23–25} was used to study the mechanistic details of the reaction between surface nitrates and C₃H₆ during the oxidation of the hydrocarbon.

2. Experimental details

The 1 wt% Pt/Al₂O₃ powder sample used was purchased from Alfa Aesar. Pt dispersion was measured using H₂ chemisorption in a Hiden Catlab micro-reactor. The catalyst was heated to 500 °C in 5% H₂ in He for 30 minutes and then 100 μL of 5% H₂ in He was pulsed into a 50 mL min^{–1} of He flow every 30 seconds, with a total of 26 pulses used. A stoichiometric ratio of two Pt

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sites per H₂ molecule was used for calculation purposes.^{26–28} The Pt/Al₂O₃ catalyst Pt dispersion was 23.1%.

In situ DRIFTS measurements were performed with a Bruker Vertex 70 FTIR spectrometer equipped with a liquid N₂-cooled detector. 25 mg of the 1.0% Pt/Al₂O₃ catalyst sample was placed in a ceramic crucible in the DRIFTS cell. The exit lines were connected to a Hiden Analytical HPR20 quadrupole mass spectrometer in order to monitor the changes of gas phase species.

Prior to the experiments, the catalyst was pre-treated by heating in Ar with a total flow rate of 50 cm³ min^{−1} up to 300 °C for 1 h and then cooled down in flowing Ar to 250 °C. The IR spectrum of the Pt/Al₂O₃ catalyst at 250 °C under flowing Ar was taken as a background. Two 4-way VICI valves were installed to allow us to switch between two gas mixtures. The first was used to switch between Ar and the gas feed and the second was used for switching between other gas components, for example, switching between NO + O₂ and C₃H₆. Kr was used as a tracer for the switching experiments. The concentrations of the reactants used were: 500 ppm NO, 5% O₂, 500 ppm C₃H₆, 0.5% Kr (when added) and Ar balance. The total flow rate was 50 cm³ min^{−1}.

Three different sets of transient switching experiments were performed. The first two sets of experiments were carried out using the short time on stream (STOS) technique.^{24,25} In these experiments the catalyst is only exposed to reactants for the shortest time possible (typically tens of seconds) so that any adsorption on the support is minimised and it is easier to distinguish between potential reactant intermediates, at or near the active metal, from those, mostly inactive, species which have similar infrared spectra, and are located at a larger distance from the active metal. In these STOS experiments we switched between NO–O₂ and C₃H₆–Kr, or between NO–O₂ and C₃H₆–O₂–Kr. The catalyst was exposed to the NO–O₂ gas feed for 1 min at 250 °C before performing fast cycling transient switches from one gas mixture to another every 1 min. For comparison, in a final set of experiments, we show a conventional long time on stream procedure using an NO–O₂ feed for 90 min, after which Ar was used to purge for 5 min before replacing this with the C₃H₆ feed. This allows us to compare the results from a conventional long exposure experiment with those from a STOS experiment.

In all cases, the *in situ* DRIFTS spectra were recorded with a resolution of 4 cm^{−1} and with the accumulation of 16 scans every 10 s during transient switches. The DRIFTS spectra were analyzed by the OPUS software. For the gas phase analysis, the following mass-to-charge (*m/z*) ratios were monitored as a function of time: 27 (C₃H₆), 28 (N₂ and CO), 30 (NO), 32 (O₂), 44 (N₂O and CO₂), 46 (NO₂) and 82 (Kr). The results for gaseous CO, N₂ (*m/z* = 28), NO₂ (*m/z* = 46) are not reported because; (1) the MS signal of *m/z* = 46 was not observed as NO₂ nearly 100% fragments to *m/z* = 30 and therefore, the MS signal at *m/z* = 30 is assigned to either NO or NO₂; and (2) because CO₂ (*m/z* = 44) is formed throughout the experiments and can be fragmented into *m/z* = 28 which then severely overlaps with the signals for CO and N₂.

3. Results and discussion

3.1 STOS experiments when switching between NO–O₂ and C₃H₆ [in the absence of O₂]

Fig. 1 shows the results obtained during the first 2 min cycle when the catalyst was exposed to the NO–O₂ mixture for just 1 min before switching to C₃H₆ for 1 min.

The NO signal gradually increased over the course of the first minute and the total amount of NO_x adsorbed was calculated to be 40.9 μmol g_{cat}^{−1} (see Table 1). When the C₃H₆ was introduced, even in the absence of gaseous O₂, it was found that the C₃H₆ was completely consumed for at least 10 s. The total amount of C₃H₆ consumed was calculated to be 18.9 μmol g_{cat}^{−1} over the course of 1 min. At the same time, CO₂ was formed and NO was released. The amount of NO_x released and CO₂ produced is 9.8 and 23.3 μmol g_{cat}^{−1}, respectively. The amount of CO₂ production was significantly smaller than that calculated from the C₃H₆ consumption using the stoichiometric reaction of 3 moles of CO₂ (56 μmol g_{cat}^{−1}) being formed from 1 mole of C₃H₆. As we shall see later from the DRIFTS experiments, some of the “missing” carbon can be accounted for by formation of CO and by carboxylate and formate species adsorbed on the support.

These data indicate that some of the C₃H₆ or an intermediate species was adsorbed on the catalyst. Further evidence for this can be seen in Fig. 1 when replacing C₃H₆ with NO–O₂. A sharp peak in CO₂ production (31.5 μmol g_{cat}^{−1}) was observed which is due to the O₂(g) + C_xH_y(ads) reaction, and the oxidation of CO(ads) and NCO(ads). In combination with the amount of CO₂ formed during the NO–O₂ pulse, this now accounts for all the carbon introduced during the C₃H₆ pulse.

The amount of NO_x adsorbed in the second cycle (see Fig. 1) was less than the amount adsorbed in the first cycle, which indicates that not all of the NO that was adsorbed in the first cycle was removed by the propene. Nevertheless, a significant

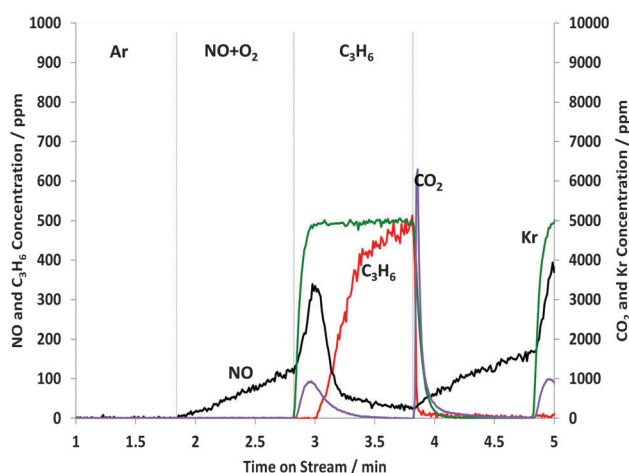


Fig. 1 Changes in the gas phase species obtained from the STOS experiment when switching from NO + O₂ to C₃H₆: outlet ¹⁴N_x and C₃H₆ concentrations as a function of time on stream during the 1st cycle of 60 s switches between NO–O₂ and C₃H₆ over 1% Pt/Al₂O₃ at 250 °C. Feed conditions: 500 ppm NO, 500 ppm C₃H₆, 5% O₂, Kr (when added) and Ar balance.



Table 1 Quantification during STOS-DRIFTS-MS experiments at 250 °C^a

Cycle no.	NO + O ₂	C ₃ H ₆			NO + O ₂	C ₃ H ₆ + O ₂		
	NO _x adsorption	NO _x desorption	C ₃ H ₆ consumption	CO ₂ formation	NO _x adsorption	NO _x desorption	C ₃ H ₆ consumption	CO ₂ formation
1	40.9	9.8	18.9	23.3	39.8	7.2	46.4	127.9
10	32.8	10.1	18.6	23.9	26.2	7.7	46.4	129.4

^a All the calculated values are reported in $\mu\text{mol g}_{\text{cat}}^{-1}$.

amount of NO still adsorbed in the second cycle. Therefore under these STOS conditions, the results indicate that C₃H₆ was indeed reacting with adsorbed NO_x species. As well as reaction with the adsorbed NO_x, some of the propene can react with PtO_x formed on exposure to the NO–O₂ mixture. It should be noted that in this switching apparatus, we can monitor the Kr switch to show that there is very little leakage of gaseous oxygen from the NO–O₂ pulse to the C₃H₆ pulse and so very little of the

C₃H₆ removed will be due to the O₂ + C₃H₆ reaction. Also, Fig. 1 shows that CO₂ formation took place for at least 40 s, compared with the disappearance of O₂ which is rapid (<12 s (not shown)) on removal of the NO–O₂ from the feed. Overall, we can confidently attribute some propene oxidation to a reaction with previously adsorbed species, of which a nitrate-type species is the most probable.

Clear confirmation that adsorbed NO_x was removed when C₃H₆ was added is seen in Fig. 2, which shows the corresponding DRIFTS spectra for these STOS experiments. When the NO–O₂ mixture was introduced to the catalyst for the first minute, the bands at 1230 cm^{−1} (nitrites) and at 1308 and 1545 cm^{−1} (nitrates) increased steadily.^{29–35} On the other hand, when the NO–O₂ stream was replaced by C₃H₆ these bands decreased in intensity and essentially disappeared after 1 min of exposure to C₃H₆. It is observed that nitrates (1308 cm^{−1}) react with C₃H₆ slightly faster than nitrites (1230 cm^{−1}). This is probably due to the fact that in a short period of 1 min a small amount of nitrates are adsorbed weakly and very close to the Pt interfaces and then can react quickly when replacing the NO–O₂ mixture with C₃H₆, whereas nitrites are formed quickly under the NO–O₂ feed, allowing some to be adsorbed slightly further away from the Pt on the support.^{34,35} However, there are no observable changes in the band at 1545 cm^{−1} due to the fact that it is swamped with bands due to carboxylate-type species forming in the same region.^{33–36} New IR bands also appeared at

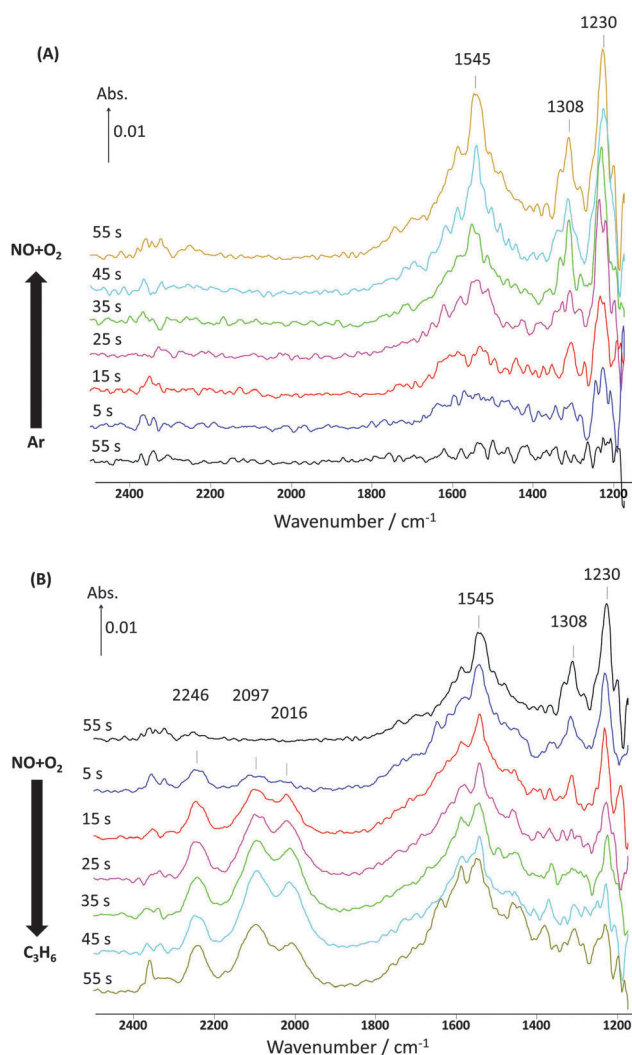


Fig. 2 Changes in the surface species corresponding to Fig. 1 obtained from the DRIFTS-MS system as a function of time on stream during the 1st cycle of 60 s switches. (A) Switch from Ar to NO + O₂ and (B) switch from NO + O₂ to C₃H₆ over 1% Pt/Al₂O₃ at 250 °C. Feed conditions: 500 ppm NO, 500 ppm C₃H₆, 5% O₂, Kr (when added) and Ar balance.

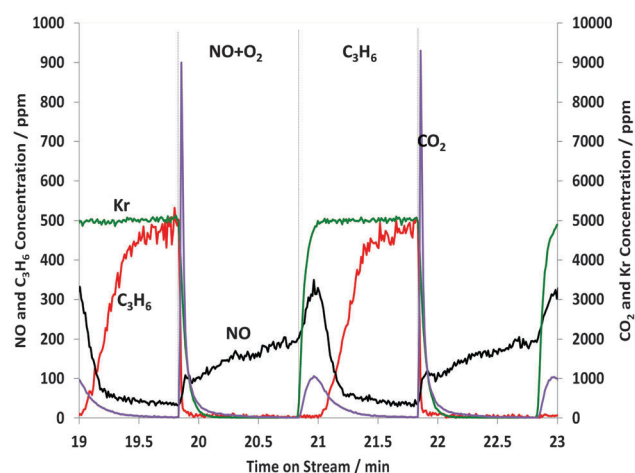


Fig. 3 Changes in the gas phase species obtained from the STOS experiment when switching from NO + O₂ to C₃H₆: outlet ¹⁴N_x and C₃H₆ concentrations as a function of time on stream during the 10th cycle of 60 s switches between NO–O₂ and C₃H₆ over 1% Pt/Al₂O₃ at 250 °C. Feed conditions: 500 ppm NO, 500 ppm C₃H₆, 5% O₂, Kr (when added) and Ar balance.



2016 and 2097, which are assigned to CO adsorbed on Pt,^{37–39} and at 2246 cm⁻¹, which is assigned to adsorbed NCO species.^{40–42} Overall, it seems clear that C₃H₆ reacted with adsorbed NO_x, which was probably in the form of a surface nitrate or nitrite.

Repeating the STOS experiment for more of the two-minute cycles, the results in the data for the tenth cycle are shown in Fig. 3.

Qualitatively, these kinetic results look similar to those seen for the first cycle, and almost identical to the results for the second cycle, as shown in Fig. 1, so again it appears that there is reaction between gaseous propene and adsorbed nitrate-type species. However, see Table 1, the calculated amount of NO_x adsorbed from the NO–O₂ feed is 32.8 μmol g_{cat}⁻¹ during the

10th cycle, compared with 40.9 μmol g_{cat}⁻¹ from the first cycle. Thus, as we increase the number of cycles we find that less nitrates are formed so presumably only a fraction of the adsorbed nitrates is being reduced by propene and the total amount of residual nitrate-type species has increased with each cycle. The amount of NO_x released and the amount of C₃H₆ consumed remained about the same at 10.1 and 18.6 μmol g_{cat}⁻¹, respectively. However, the DRIFTS experiments presented in Fig. 4 for the 10th cycle appear to be contrast with this information.

The DRIFTS results in Fig. 4 show how the amount of retained surface nitrates changed as we increased the number of two-minute cycles. By the tenth two-minute cycle, there was essentially no change in the DRIFTS spectra. No significant changes in the nitrate bands were observed either on exposure to the NO–O₂ mixture or to the C₃H₆. The surface had apparently become saturated with essentially inactive nitrate and nitrite species. The band at 1457 cm⁻¹ and the unresolved bands between 1397 and 1370 cm⁻¹, that are attributed to acetate-type species and formate-type species, respectively,^{33–36} showed a similar lack of change when the gas atmosphere was changed. Note, however, that the bands attributed to CO (2097 and 2016 cm⁻¹) were removed by the NO–O₂ pulse which is consistent with oxidation of intermediate CO adsorbed on the Pt and the reoxidation of the Pt during this pulse.

It is clear that exposure of the catalyst to the reaction mixtures for as little as 20 minutes in total took the experiment beyond the point where active surface species can be detected and their concentrations monitored. Already the active nitrates, as previously seen to be reactive under the STOS conditions and shown in Fig. 2, were swamped by spectroscopically similar inactive species, presumably due to nitrates that formed on the support but which are not close enough to the metal to be catalytically important. These species were inactive, or at least had an activity that was much lower than that found for the

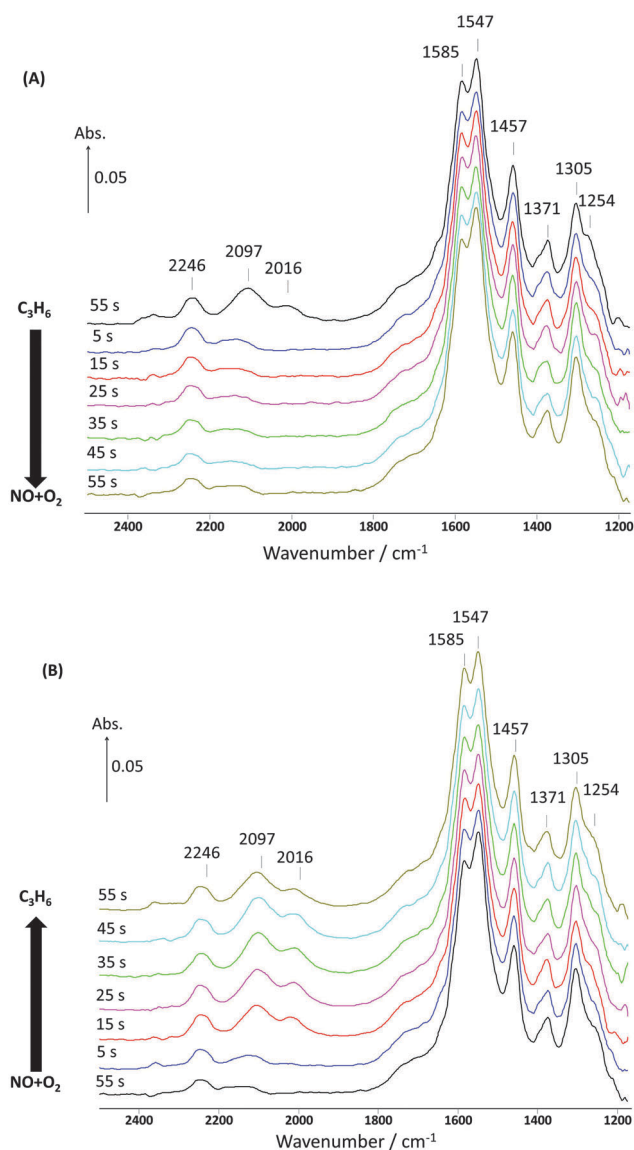


Fig. 4 Changes in the surface species corresponding to Fig. 3 and obtained from the DRIFTS-MS system as a function of time on stream during the 10th cycle of 60 s switches. (A) Switch from C₃H₆ to NO + O₂ and (B) switch from NO + O₂ to C₃H₆ over 1% Pt/Al₂O₃ at 250 °C. Feed conditions: 500 ppm NO, 500 ppm C₃H₆, 5% O₂, Kr (when added) and Ar balance.

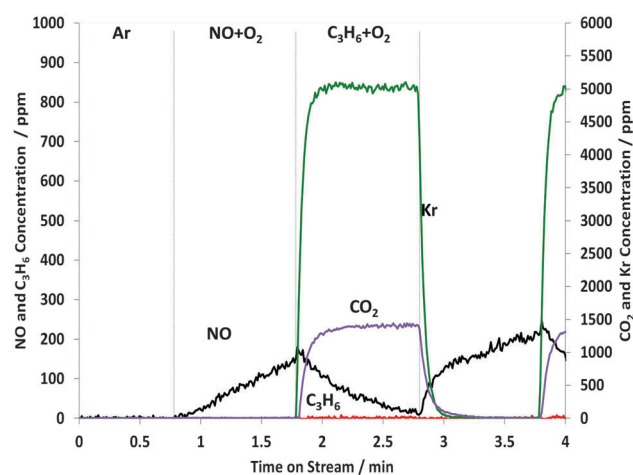


Fig. 5 Changes in the gas phase species obtained from the STOS experiment when switching from NO + O₂ to C₃H₆ + O₂: outlet ¹⁴N₂O_x and C₃H₆ concentrations as a function of time on stream during the 1st cycle of 60 s switches between NO–O₂ and C₃H₆–O₂ over Pt/Al₂O₃ at 250 °C. Feed conditions: 500 ppm NO, 500 ppm C₃H₆, 5% O₂, Kr (when added) and Ar balance.



“active” intermediates observed in the first cycle. These STOS experiments showed that there was a reaction between adsorbed nitrate-type species and gaseous propene. However, the ability to detect and monitor these surface reactions was lost after only a few two-minute cycles of the reactants.

3.2 STOS experiments with switching between NO–O₂ and C₃H₆–O₂ [in the presence of O₂]

The effect of including oxygen with the propene in the STOS switching experiments is shown in Fig. 5. In contrast to the experiments in the absence of oxygen, complete combustion of C₃H₆ (46.4 $\mu\text{mol g}_{\text{cat}}^{-1}$) was observed and summarised in Table 1. However, during the first 1 minute cycle under C₃H₆–O₂ feed, 127.9 $\mu\text{mol g}_{\text{cat}}^{-1}$ of gas phase CO₂ was produced which is less than the 139.2 $\mu\text{mol g}_{\text{cat}}^{-1}$, calculated using the stoichiometric reaction of 3 moles of CO₂ formed from 1 mole of C₃H₆.

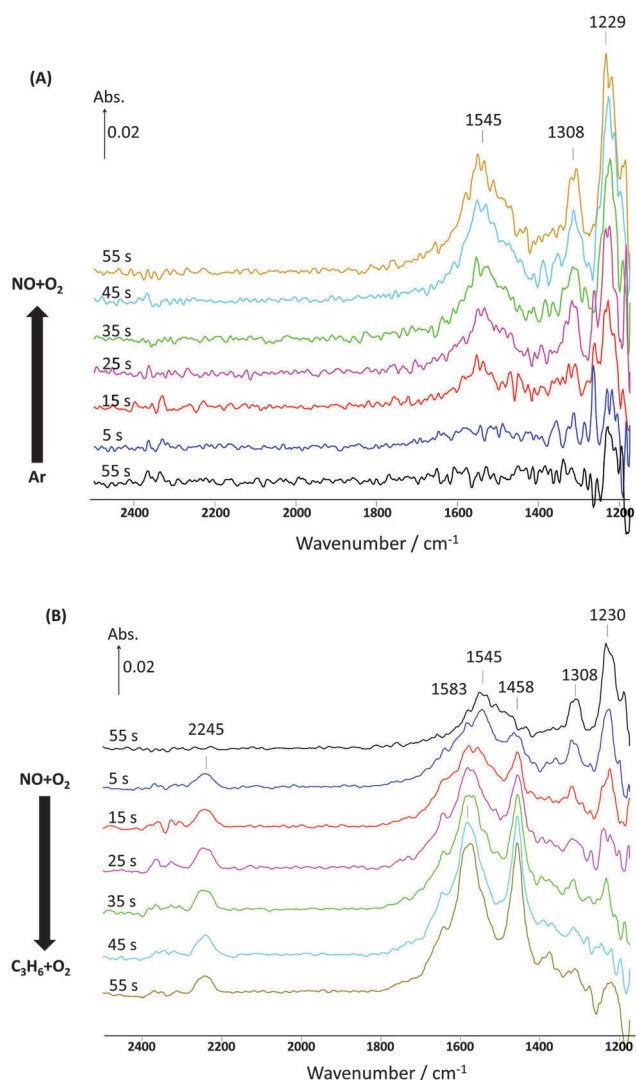


Fig. 6 Changes in the surface species corresponding to Fig. 5 and obtained from the DRIFTS-MS system as a function of time on stream during the 1st cycle of 60 s switches. (A) Switch from Ar to NO + O₂ and (B) switch from NO + O₂ to C₃H₆ + O₂ over 1% Pt/Al₂O₃ at 250 °C. Feed conditions: 500 ppm NO, 500 ppm C₃H₆, 5% O₂, Kr (when added) and Ar balance.

This is due to the formation and subsequent adsorption of acetate and carbonate species (see Fig. 6). On the other hand, the calculated amount of NO_x adsorbed was 39.8 $\mu\text{mol g}_{\text{cat}}^{-1}$ which is essentially identical to the amount found in the absence of oxygen, although comparison of Fig. 1 and 5 shows that the NO_x profile was quite different when NO was replaced by C₃H₆–O₂ rather than C₃H₆ alone. However, once again, it seems that some of the surface NO_x species can react with propene even when excess oxygen was present in the C₃H₆–O₂ mixture.

Importantly, as shown in Table 1, the amount of NO_x desorbed under the C₃H₆ + O₂ feed in the first cycle when O₂ was present with the C₃H₆ is 7.2 $\mu\text{mol g}_{\text{cat}}^{-1}$ which contrasts with the 9.8 $\mu\text{mol g}_{\text{cat}}^{-1}$ of NO_x desorbed when O₂ was not added to the C₃H₆. This would seem to indicate that there is less direct reaction between adsorbed NO and the C₃H₆ in the case where there is O₂ in the gas phase. If correct, this would indicate that either the reoxidation of the Pt by O₂, followed by the reaction between PtO_x and C₃H₆ is faster than the direct reaction between C₃H₆ and adsorbed NO_x, or that the nitrate species are more stable in the presence of O₂. The latter is consistent with literature describing NO_x adsorption on Pt/Ba/Al₂O₃ materials.^{43,44}

Further evidence that there is still some reaction with adsorbed NO_x can be seen in the DRIFTS spectra shown in Fig. 6. These results for the first two-minute cycle show that when replacing NO–O₂ with C₃H₆–O₂, surface nitrites (1230 cm^{−1}) and nitrates (1308 cm^{−1}) were removed. It was also observed that carboxylate peaks (1458 and 1583 cm^{−1}) appeared from the partial oxidation of C₃H₆ by O₂ or NO_x. This demonstrates that nitrate stability is not limiting the reaction.

During the 10th cycle, Fig. 7 and Table 1 show that the amount of NO_x adsorption (26.2 $\mu\text{mol g}_{\text{cat}}^{-1}$) under the NO–O₂ feed becomes smaller due to more adsorbed NO being retained from the earlier cycles (compare cycle 1 in Fig. 5), and/or because of some residual oxidation of the Pt blocking NO_x uptake.

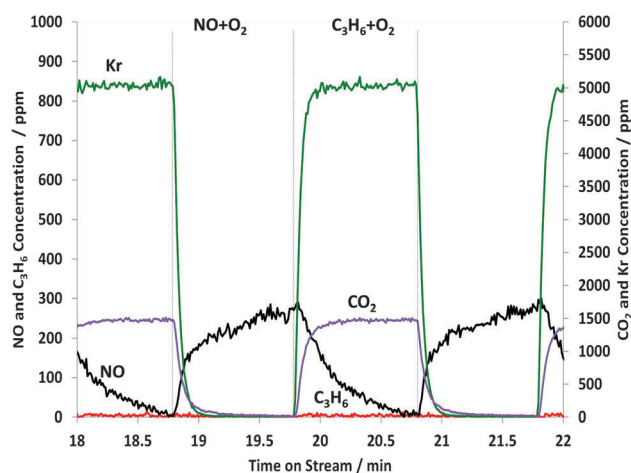


Fig. 7 Changes in the gas phase species obtained from the STOS experiment when switching from NO + O₂ to C₃H₆ + O₂: outlet ¹⁴N₂O_x and C₃H₆ concentrations as a function of time on stream during the 10th cycle of 60 s switches between NO + O₂ and C₃H₆ + O₂ over 1% Pt/Al₂O₃ at 250 °C. Feed conditions: 500 ppm NO, 500 ppm C₃H₆, 5% O₂, Kr (when added) and Ar balance.



Again, it is seen that, when replacing with $\text{C}_3\text{H}_6\text{-O}_2$, the NO signal slowly decreased and the amount of NO_x desorbed was $7.7 \mu\text{mol g}_{\text{cat}}^{-1}$, which is the same within experimental error to the amount seen in the first cycle. However, there was no significant change in the infrared bands for the nitrates as can be seen in Fig. 8.

Once again, in this case with O_2 added to the C_3H_6 , we find that even after as few as ten two-minute exposures to the reaction mixtures it becomes impossible to obtain any useful information from the DRIFTS results. On the other hand, using the STOS technique we can clearly demonstrate the removal of adsorbed nitrates, and the production of gaseous NO_x , when a $\text{C}_3\text{H}_6\text{-O}_2$ mixture was passed over a Pt catalyst that had

previously been exposed to a NO-O_2 mixture. These results also help clarify an apparent discrepancy in previous data.⁴⁵ These showed for propene oxidation that the activation energy associated with nitrates as oxidant is significantly lower than that for O_2 as oxidant but there were only slight improvements in the rate of propene oxidation when nitrates were present.⁴⁵ These STOS data indicate that this is due to the relatively small amount of reactive nitrates (likely residing near the Pt) compared to the abundant nitrate species that form over the support.

3.3 Conventional long time on stream experiments with switching from NO-O_2 to Ar to C_3H_6

The critical role of the surface nitrates in the oxidation of the hydrocarbon is not obvious from an examination of “conventional” long time on stream experiments. In this case, the Pt catalyst was exposed to the $\text{NO} + \text{O}_2$ feed for 90 min, followed by

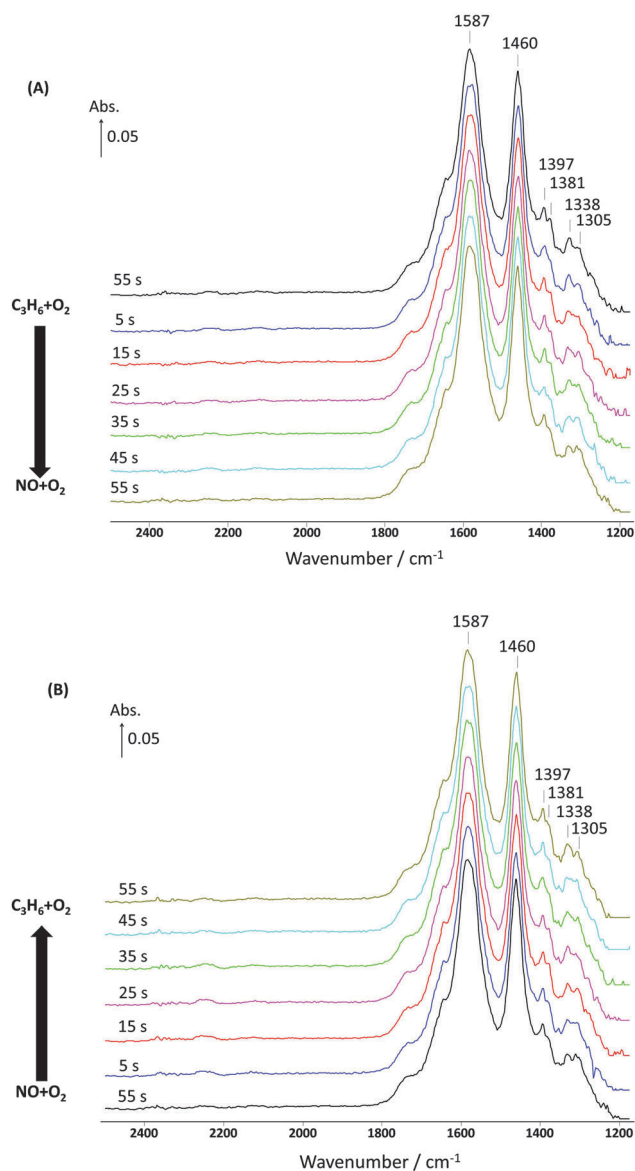


Fig. 8 Changes in the surface species corresponding to Fig. 7 and obtained from the DRIFTS-MS system as a function of time on stream during the 10th cycle of 60 s switches. (A) Switch from $\text{C}_3\text{H}_6 + \text{O}_2$ to $\text{NO} + \text{O}_2$ and (B) switch from $\text{NO} + \text{O}_2$ to $\text{C}_3\text{H}_6 + \text{O}_2$ over 1% Pt/ Al_2O_3 at 250 °C. Feed conditions: 500 ppm NO, 500 ppm C_3H_6 , 5% O_2 , Kr (when added) and Ar balance.

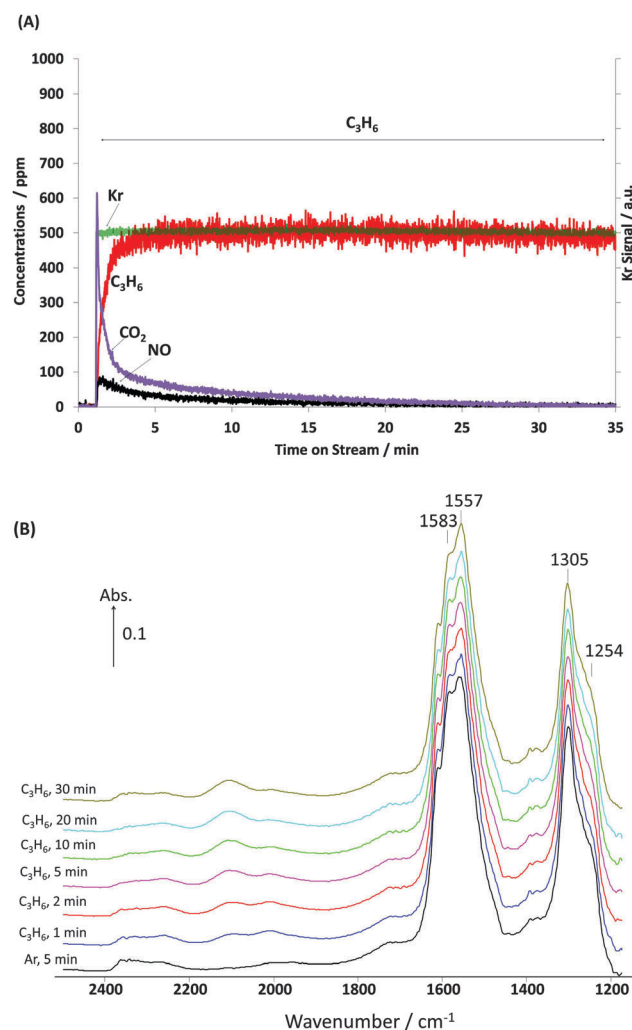


Fig. 9 Changes in (A) gas phase and (B) surface species obtained from a “conventional” steady state (long time on stream) transient experiment as a function of time on stream over the course of 30 min under C_3H_6 flow over 1% Pt/ Al_2O_3 at 250 °C. Feed conditions: 500 ppm NO, 500 ppm C_3H_6 , 5% O_2 , Kr (when added) and Ar balance.



Ar for 5 min and then by C₃H₆. Over a period of 90 min the surface nitrate and nitrite bands developed continuously (Fig. S1, ESI†). Using Ar as a purge will clarify whether or not a fraction of adsorbed NO_x can be decomposed or desorbed into gas phase. After switching to inert Ar to flush the catalyst (Fig. S2, ESI†), it is shown that there was essentially no change in the surface nitrate or nitrite bands as well as gas phase NO_x (not shown).

In addition, Fig. 9A clearly shows that after switching to C₃H₆ both gas phase NO_x and CO₂ were rapidly released due to the interaction between adsorbed NO_x and C₃H₆. However, it is important to note that although changes in the gas phase species were observed, which demonstrate that some adsorbed nitrate-type species were reacting with C₃H₆, the DRIFT spectra in Fig. 9B were unchanged even after 30 min exposure to C₃H₆. Clearly, under these “traditional” transient experimental conditions virtually all the infrared detectable nitrates and nitrites were inactive.

4. Conclusions

The contribution of surface nitrate-type species to the oxidation of propene over a Pt diesel oxidation catalyst has been demonstrated unequivocally for the first time both for propene-only and propene + oxygen reaction mixtures. The use of the Short Time on Stream (STOS) transient kinetic technique has allowed the identification of a surface nitrate-type species that can react with propene to produce CO₂ and NO_x. The STOS results show that after long times on stream most of the nitrate-type species that are detectable by DRIFTS are either unreactive or have a very low reactivity. The benefit of using the STOS transient technique is the ability to clearly differentiate between unreactive spectator species and reactive intermediates.

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