PAPER

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 NO_2 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 NO_2, the so-called fast SCR reaction,[3,4] and NSR catalysts trap NO_2 more readily than NO,[5–9] thereby improving NO_x storage performance[10–13] as the engine out ratios of $NO : NO_2$ are typically high. The formed NO_2 can also oxidize soot at significantly lower temperatures than O_2.[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 NO_2 is also involved in the oxidation of CO and hydrocarbons over the DOC. Under certain circumstances, NO_2 has been shown to be preferentially consumed relative to O_2 in the oxidation reaction.[14,15] This leads to no NO_2 observed until all, or most, of the CO and hydrocarbons are oxidized and it is only after they are combusted is NO_2 observed. Katare and co-workers[22] 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 H_2-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/Al_2O_3 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 C_3H_6 during the oxidation of the hydrocarbon.

2. Experimental details

The 1 wt% Pt/Al_2O_3 powder sample used was purchased from Alfa Aesar. Pt dispersion was measured using H_2 chemisorption in a Hiden Catlab micro-reactor. The catalyst was heated to 500 °C in 5% H_2 in He for 30 minutes and then 100 µL of 5% H_2 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 H_2 molecule was used for calculation purposes.[26–28] The Pt/Al$_2$O$_3$ catalyst Pt dispersion was 23.1%.

In situ DRIFTS measurements were performed with a Bruker Vertex 70 FTIR spectrometer equipped with a liquid N$_2$-cooled detector. 25 mg of the 1.0% Pt/Al$_2$O$_3$ 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 cm^3 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/Al$_2$O$_3$ 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 + O$_2$ and C$_3$H$_6$. Kr was used a tracer for the switching experiments. The concentrations of the reactants used were: 500 ppm NO, 5% O$_2$, 500 ppm C$_3$H$_6$, 0.5% Kr (when added) and Ar balance. The total flow rate was 50 cm^3 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–O$_2$ and C$_3$H$_6$–Kr, or between NO–O$_2$ and C$_3$H$_6$–O$_2$–Kr. The catalyst was exposed to the NO–O$_2$ 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–O$_2$ feed for 90 min, after which Ar was used to purge for 5 min before replacing this with the C$_3$H$_6$ 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 (C$_3$H$_6$), 28 (N$_2$ and CO), 30 (NO), 32 (O$_2$), 44 (N$_2$O and CO$_2$), 46 (NO$_2$) and 82 (Kr). The results for gaseous CO, N$_2$ (*m/z* = 28), NO$_2$ (*m/z* = 46) are not reported because; (1) the MS signal of *m/z* = 46 was not observed as NO$_2$ nearly 100% fragments to *m/z* = 30 and therefore, the MS signal at *m/z* = 30 is assigned to either NO or NO$_x$; and (2) because CO$_2$ (*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 N$_2$.

3. Results and discussion

3.1 STOS experiments when switching between NO–O$_2$ and C$_3$H$_6$ [in the absence of O$_2$]

Fig. 1 shows the results obtained during the first 2 min cycle when the catalyst was exposed to the NO–O$_2$ mixture for just 1 min before switching to C$_3$H$_6$ 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 C$_3$H$_6$ was introduced, even in the absence of gaseous O$_2$, it was found that the C$_3$H$_6$ was completely consumed for at least 10 s. The total amount of C$_3$H$_6$ consumed was calculated to be 18.9 μmol g$_{cat}^{-1}$ over the course of 1 min. At the same time, CO$_2$ was formed and NO was released. The amount of NO$_x$ released and CO$_2$ produced is 9.8 and 23.3 μmol g$_{cat}^{-1}$, respectively. The amount of CO$_2$ production was significantly smaller than that calculated from the C$_3$H$_6$ consumption using the stoichiometric reaction of 3 moles of CO$_2$ (56 μmol g$_{cat}^{-1}$) being formed from 1 mole of C$_3$H$_6$. 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 C$_3$H$_6$ or an intermediate species was adsorbed on the catalyst. Further evidence for this can be seen in Fig. 1 when replacing C$_3$H$_6$ with NO–O$_2$. A sharp peak in CO$_2$ production (31.5 μmol g$_{cat}^{-1}$) was observed which is due to the O$_2$(g) + C$_x$H$_y$(ads) reaction, and the oxidation of CO(ads) and NCO(ads). In combination with the amount of CO$_2$ formed during the NO–O$_2$ pulse, this now accounts for all the carbon introduced during the C$_3$H$_6$ 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
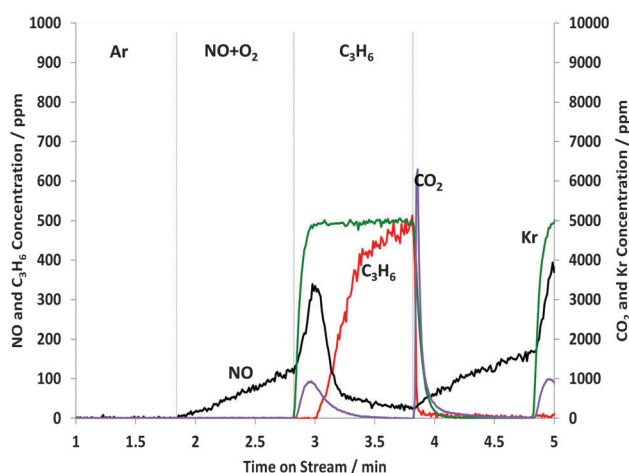
Fig. 1 Changes in the gas phase species obtained from the STOS experiment when switching from NO + O$_2$ to C$_3$H$_6$: outlet ^{14}NO$_x$ and C$_3$H$_6$ concentrations as a function of time on stream during the 1st cycle of 60 s switches between NO–O$_2$ and C$_3$H$_6$ over 1% Pt/Al$_2$O$_3$ at 250 °C. Feed conditions: 500 ppm NO, 500 ppm C$_3$H$_6$, 5% O$_2$, Kr (when added) and Ar balance.

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

| Cycle no. | NO + O_2 | C_3H_6 | | | NO + O_2 | C_3H_6 + O_2 | | |
	NO_x adsorption	NO_x desorption	C_3H_6 consumption	CO_2 formation	NO_x adsorption	NO_x desorption	C_3H_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

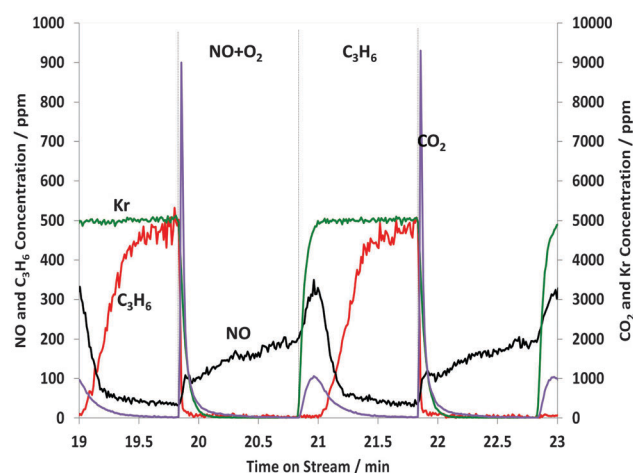[a] All the calculated values are reported in μmol g_{cat}^{-1}.

amount of NO still adsorbed in the second cycle. Therefore under these STOS conditions, the results indicate that C_3H_6 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–O_2 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–O_2 pulse to the C_3H_6 pulse and so very little of the

C_3H_6 removed will be due to the O_2 + C_3H_6 reaction. Also, Fig. 1 shows that CO_2 formation took place for at least 40 s, compared with the disappearance of O_2 which is rapid (<12 s (not shown)) on removal of the NO–O_2 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 C_3H_6 was added is seen in Fig. 2, which shows the corresponding DRIFTS spectra for these STOS experiments. When the NO–O_2 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–O_2 stream was replaced by C_3H_6 these bands decreased in intensity and essentially disappeared after 1 min of exposure to C_3H_6. It is observed that nitrates (1308 cm^{-1}) react with C_3H_6 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–O_2 mixture with C_3H_6, whereas nitrites are formed quickly under the NO–O_2 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
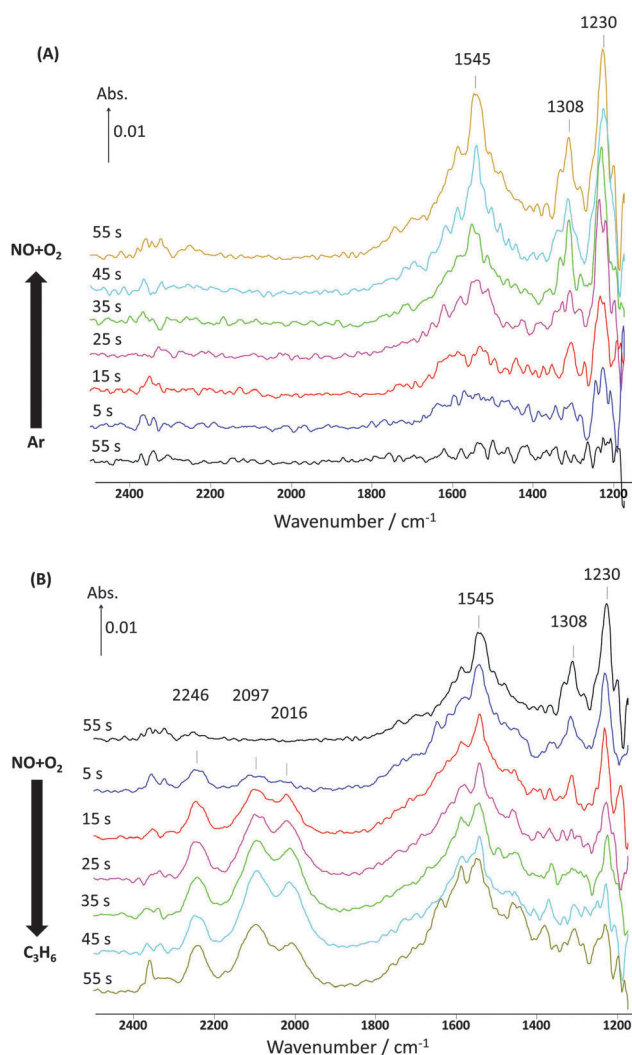
Fig. 2 Changes in the surface species corresponding to Fig. 1 obtained from the DRIFTS-MS system as a function of time on stream during the 1st cycle of 60 s switches. (A) Switch from Ar to NO + O_2 and (B) switch from NO + O_2 to C_3H_6 over 1% Pt/Al$_2$O$_3$ at 250 °C. Feed conditions: 500 ppm NO, 500 ppm C_3H_6, 5% O_2, Kr (when added) and Ar balance.

Fig. 3 Changes in the gas phase species obtained from the STOS experiment when switching from NO + O_2 to C_3H_6: outlet $^{14}NO_x$ and C_3H_6 concentrations as a function of time on stream during the 10th cycle of 60 s switches between NO–O_2 and C_3H_6 over 1% Pt/Al$_2$O$_3$ at 250 °C. Feed conditions: 500 ppm NO, 500 ppm C_3H_6, 5% O_2, Kr (when added) and Ar balance.

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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 C_3H_6 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 $NO-O_2$ 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 C_3H_6 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 $NO-O_2$ mixture or to the C_3H_6. 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 $NO-O_2$ 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
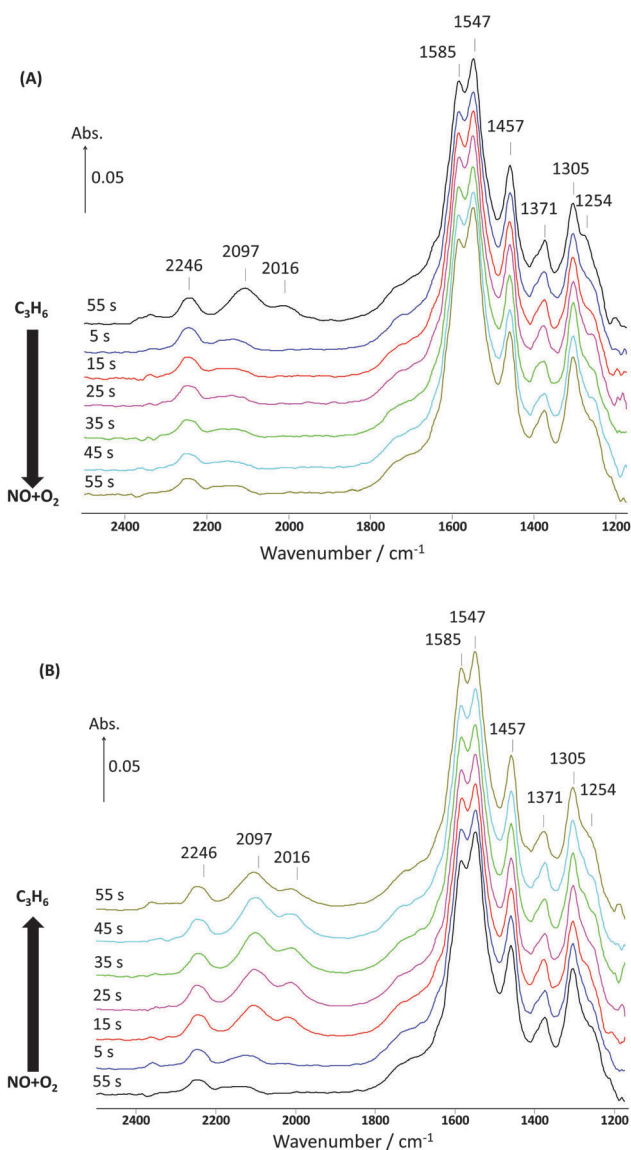
Fig. 4 Changes in the surface species corresponding to Fig. 3 and obtained from the DRIFTS-MS system as a function of time on stream during the 10th cycle of 60 s switches. (A) Switch from C_3H_6 to $NO + O_2$ and (B) switch from $NO + O_2$ to C_3H_6 over 1% Pt/Al$_2$O$_3$ at 250 °C. Feed conditions: 500 ppm NO, 500 ppm C_3H_6, 5% O_2, Kr (when added) and Ar balance.
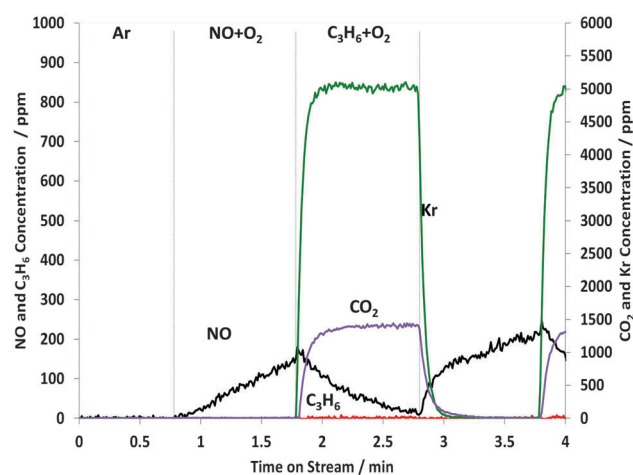
Fig. 5 Changes in the gas phase species obtained from the STOS experiment when switching from $NO + O_2$ to $C_3H_6 + O_2$: outlet $^{14}NO_x$ and C_3H_6 concentrations as a function of time on stream during the 1st cycle of 60 s switches between $NO-O_2$ and $C_3H_6-O_2$ over Pt/Al$_2$O$_3$ at 250 °C. Feed conditions: 500 ppm NO, 500 ppm C_3H_6, 5% O_2, Kr (when added) and Ar balance.

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"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–O_2 and C_3H_6–O_2 [in the presence of O_2]

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 C_3H_6 (46.4 µmol g_{cat}^{-1}) was observed and summarised in Table 1. However, during the first 1 minute cycle under C_3H_6–O_2 feed, 127.9 µmol g_{cat}^{-1} of gas phase CO_2 was produced which is less than the 139.2 µmol g_{cat}^{-1}, calculated using the stoichiometric reaction of 3 moles of CO_2 formed from 1 mole of C_3H_6.
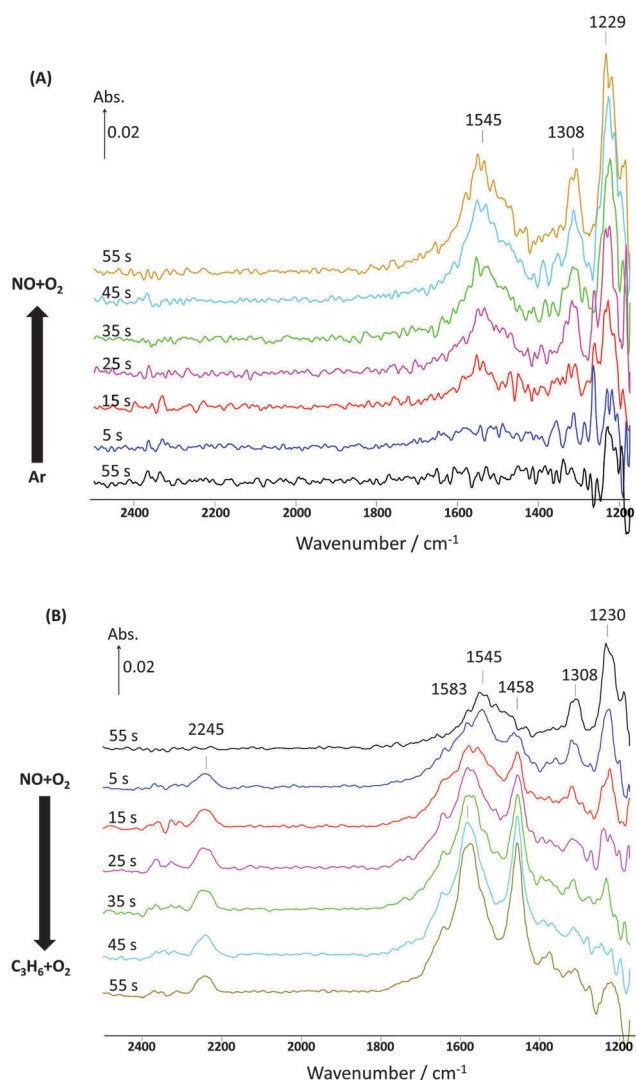
This is due to the formation and subsequent adsorption of acetate and carbonate species (see Fig. 6). On the other hand, the calculated amount of NO_x adsorbed was 39.8 µmol g_{cat}^{-1} which is essentially identical to the amount found in the absence of oxygen, although comparison of Fig. 1 and 5 shows that the NO_x profile was quite different when NO was replaced by C_3H_6–O_2 rather than C_3H_6 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 C_3H_6–O_2 mixture.

Importantly, as shown in Table 1, the amount of NO_x desorbed under the $C_3H_6 + O_2$ feed in the first cycle when O_2 was present with the C_3H_6 is 7.2 µmol g_{cat}^{-1} which contrasts with the 9.8 µmol g_{cat}^{-1} of NO_x desorbed when O_2 was not added to the C_3H_6. This would seem to indicate that there is less direct reaction between adsorbed NO and the C_3H_6 in the case where there is O_2 in the gas phase. If correct, this would indicate that either the reoxidation of the Pt by O_2, followed by the reaction between PtO_x and C_3H_6 is faster than the direct reaction between C_3H_6 and adsorbed NO_x, or that the nitrate species are more stable in the presence of O_2. The latter is consistent with literature describing NO_x adsorption on Pt/Ba/Al_2O_3 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–O_2 with C_3H_6–O_2, 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 C_3H_6 by O_2 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 µmol g_{cat}^{-1}) under the NO–O_2 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.
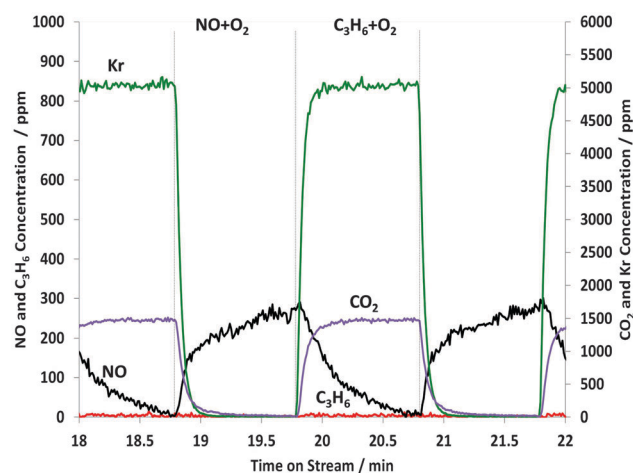

Fig. 6 Changes in the surface species corresponding to Fig. 5 and obtained from the DRIFTS-MS system as a function of time on stream during the 1st cycle of 60 s switches. (A) Switch from Ar to NO + O_2 and (B) switch from NO + O_2 to C_3H_6 + O_2 over 1% Pt/Al_2O_3 at 250 °C. Feed conditions: 500 ppm NO, 500 ppm C_3H_6, 5% O_2, Kr (when added) and Ar balance.

Fig. 7 Changes in the gas phase species obtained from the STOS experiment when switching from NO + O_2 to C_3H_6 + O_2: outlet $^{14}NO_x$ and C_3H_6 concentrations as a function of time on stream during the 10th cycle of 60 s switches between NO + O_2 and C_3H_6 + 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.

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Again, it is seen that, when replacing with C_3H_6–O_2, the NO signal slowly decreased and the amount of NO_x desorbed was 7.7 µmol g_{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 C_3H_6–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 NO + O_2 feed for 90 min, followed by
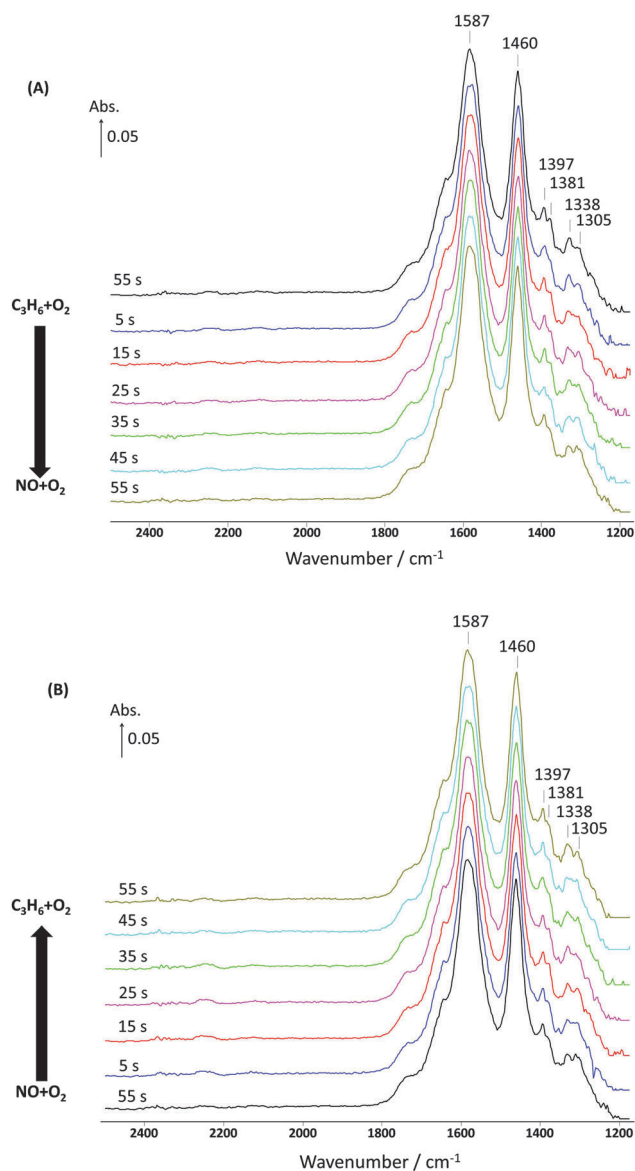
Fig. 8 Changes in the surface species corresponding to Fig. 7 and obtained from the DRIFTS-MS system as a function of time on stream during the 10th cycle of 60 s switches. (A) Switch from C_3H_6 + O_2 to NO + O_2 and (B) switch from NO + O_2 to C_3H_6 + O_2 over 1% Pt/Al$_2$O$_3$ at 250 °C. Feed conditions: 500 ppm NO, 500 ppm C_3H_6, 5% O_2, Kr (when added) and Ar balance.
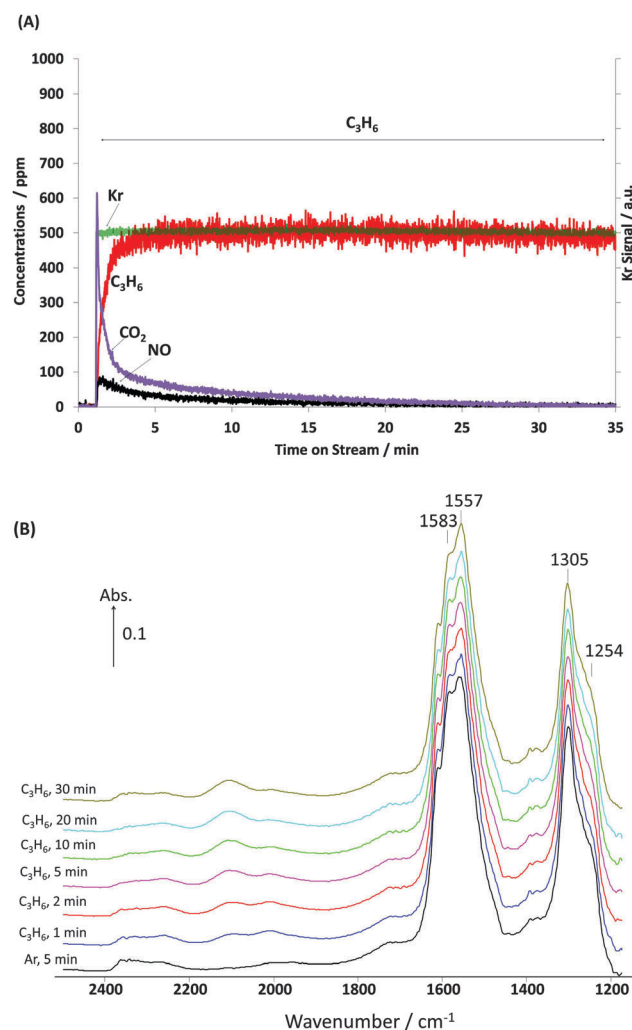
Fig. 9 Changes in (A) gas phase and (B) surface species obtained from a "conventional" steady state (long time on stream) transient experiment as a function of time on stream over the course of 30 min under C_3H_6 flow over 1% Pt/Al$_2$O$_3$ at 250 °C. Feed conditions: 500 ppm NO, 500 ppm C_3H_6, 5% O_2, Kr (when added) and Ar balance.

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Ar for 5 min and then by C_3H_6. 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 C_3H_6 both gas phase NO_x and CO_2 were rapidly released due to the interaction between adsorbed NO_x and C_3H_6. 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 C_3H_6, the DRIFT spectra in Fig. 9B were unchanged even after 30 min exposure to C_3H_6. 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 CO_2 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.

Acknowledgements

References

1 L. Castoldi, R. Matarrese, L. Lietti and P. Forzatti, *Appl. Catal., B*, 2006, **64**, 25.

2 M. Koebel, M. Elsener and G. Madia, *Ind. Eng. Chem. Res.*, 2001, **40**, 52.

3 A. Kato, S. Matsuda, T. Kamo, F. Nakajima, H. Kuroda and T. Narita, *J. Phys. Chem.*, 1981, **85**, 4099.

4 A. Grossale, I. Nova, E. Tronconi, D. Chatterjee and M. Weibel, *J. Catal.*, 2008, **256**, 312.

5 S. Erkfeld, E. Jonson and M. Larsson, *Top. Catal.*, 2001, **16–17**, 127.

6 F. Rodrigues, L. Juste, C. Potvin, J. F. Tempere, G. Blanchard and G. Djega-Mariadassou, *Catal. Lett.*, 2001, **72**, 59.

7 N. W. Cant and M. J. Patterson, *Catal. Today*, 2002, **73**, 271.

8 S. Hodjati, P. Bernhardt, C. Petit, V. Pitchon and A. Kiennemann, *Appl. Catal., B*, 1998, **19**, 2098.

9 S. Hodjati, K. Vaezzadeh, C. Petit, V. Pitchon and A. Kiennemann, *Catal. Today*, 2000, **59**, 323.

10 W. S. Epling, L. E. Campbell, A. Yezerets, N. W. Currier and J. E. Parks, *Catal. Rev.*, 2004, **46**, 163.

11 S. Salasc, M. Skoglundh and E. Fridell, *Appl. Catal., B*, 2202, **36**, 145.

12 H. Mahzoul, J. F. Brilhac and P. Gilot, *Appl. Catal., B*, 1999, **20**, 47.

13 F. Pronetto, G. Ghiotti, I. Nova, L. Lietti, E. Tronconi and P. Forzatti, *J. Phys. Chem. B*, 2001, **105**, 12732.

14 K. Irani, W. S. Epling and R. Blint, *Appl. Catal., B*, 2009, **92**, 422.

15 H. Oh, J. Luo and W. S. Epling, *Catal. Lett.*, 2011, **141**, 1746.

16 J.-H. Lee and H. H. Kung, *Catal. Lett.*, 1998, **51**, 1.

17 E. Xue, K. Seshan and J. R. H. Ross, *Appl. Catal., B*, 1996, **11**, 65.

18 P. Denton, A. Gioir-Fendler, H. Praliaud and M. Primet, *J. Catal.*, 2000, **189**, 410.

19 L. Olsson and E. Fridell, *J. Catal.*, 2002, **210**, 340.

20 S. Bernard, L. Retailleau, F. Gaillard, P. Vernoux and A. Giroir-Fendler, *Appl. Catal., B*, 2005, **55**, 11.

21 L. Olsson, M. Abul-Milh, H. Karlsson, E. Jobson, P. Thormaehlen and A. Hinz, *Top. Catal.*, 2004, **30/31**, 85.

22 S. R. Katare, J. E. Patterson and P. M. Laing, SAE paper 2007-01-3984, 2009.

23 S. Chansai, R. Burch, C. Hardacre, J. Breen and F. Meunier, *J. Catal.*, 2011, **281**, 98.

24 S. Chansai, R. Burch and C. Hardacre, *J. Catal.*, 2012, **295**, 223.

25 S. Chansai, R. Burch, C. Hardacre, J. Breen and F. Meunier, *J. Catal.*, 2010, **276**, 49.

26 J. Freel, *J. Catal.*, 1971, **25**, 139.

27 H. L. Gruber, *J. Phys. Chem.*, 1962, **66**, 54.

28 J. Dawody, L. Eurenius, H. Abdulhamid, M. Skoglundh, E. Olsson and E. Fridell, *Appl. Catal., A*, 2005, **296**, 157.

29 Y. Ji, T. J. Toops, J. A. Pihl and M. Crocker, *Appl. Catal., B*, 2009, **91**, 329.

30 T. J. Toops, D. B. Smith and W. P. Partridge, *Catal. Today*, 2006, **114**, 112.

31 B. Westerberg and E. Fridell, *J. Mol. Catal. A: Chem.*, 2001, **165**, 249.

32 C. Sedlmair, K. Seshan, A. Jentys and J. A. Lercher, *J. Catal.*, 2003, **214**, 308.

33 W. S. Epling, C. H. F. Peden and J. Szanyi, *J. Phys. Chem. C*, 2008, **112**, 10952.

34 F. C. Meunier, J. P. Breen, V. Zuzaniuk, M. Olsson and J. R. H. Ross, *J. Catal.*, 1999, **187**, 493.

35 F. C. Meunier, V. Zuzaniuk, J. P. Breen, M. Olsson and J. R. H. Ross, *Catal. Today*, 2000, **59**, 287.

36 K. Shimizu, H. Kawabata, A. Satsuma and T. Hattori, *J. Phys. Chem. B*, 1999, **103**, 5240.

37 M. Haneda, M. Sasaki, H. Hamada and M. Ozawa, *Catal. Lett.*, 2001, **141**, 1262.

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Catal. Sci. Technol., 2013, **3**, 2349–2356 | **2355**

38 G. Busca, E. Finocchio and V. S. Escribana, *Appl. Catal., B*, 2012, **113–114**, 172.

39 M. M. Schubert, M. J. Khalich, H. A. Gasteiger and R. J. Behm, *J. Power Sources*, 1999, **84**, 175.

40 N. Bion, J. Saussey, C. Hedouin, T. Seguelong and M. Daturi, *Phys. Chem. Chem. Phys.*, 2001, **3**, 4811.

41 N. Bion, J. Saussey, M. Haneda and M. Daturi, *J. Catal.*, 2003, **217**, 47.

42 B. Wichterlová, P. Sazama, J. P. Breen, R. Burch, C. J. Hill, L. Čapek and Z. Sobalík, *J. Catal.*, 2005, **235**, 195.

43 J. Anderson, A. Paterson and M. Fernandez-Garcia, *Stud. Surf. Sci. Catal.*, 2000, **130**, 1331.

44 K. Eguchi and T. Hayashi, *Catal. Today*, 1998, **45**, 109.

45 H. Oh, I. S. Pieta, J. Luo and W. S. Epling, Reaction kinetics of C_3H_6 oxidation for various reaction pathways over diesel oxidation catalysts, *Top. Catal.*, 2013, in press.