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Cite this: DOI: 10.1039/c0xx00000x

ARTICLE TYPE

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## On the role of H<sub>2</sub> to modify surface NO<sub>x</sub> species over Ag-Al<sub>2</sub>O<sub>3</sub> as lean NO<sub>x</sub> reduction catalyst: TPD and DRIFTS studies

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Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

Formation and stability of surface NO<sub>x</sub> species related to the promotional effect of H<sub>2</sub> over Ag-Al<sub>2</sub>O<sub>3</sub> as NO<sub>x</sub> reduction catalyst were investigated with temperature-programmed desorption and DRIFT spectroscopy. Formation of two groups of surface NO<sub>x</sub> species was found: a less thermally stable group of “low temperature (LT) species” and a more thermally stable group of “high temperature (HT) species”.

The LT NO<sub>x</sub> was attributable to the decomposition of surface NO<sub>x</sub> species formed on the active sites where its elimination by addition of H<sub>2</sub> or thermal decomposition correlated with higher NO oxidation and NO<sub>x</sub> reduction conversion. Under reaction conditions, these possibly inhibiting LT NO<sub>x</sub> species were stable up to about 300°C and their formation depended on donation of oxygen from surface oxides. Removal of LT nitrate species by H<sub>2</sub> accounted for only a fraction of the increased NO oxidation and NO<sub>x</sub> reduction conversion by co-feeding H<sub>2</sub>. Furthermore, it was also found that H<sub>2</sub> facilitates formation of HT NO<sub>x</sub> that primarily corresponded to the decomposition of spectator species on the Al<sub>2</sub>O<sub>3</sub> support identified as monodentate nitrate species. From TPD studies of C<sub>3</sub>H<sub>6</sub>-SCR, it was shown that H<sub>2</sub> not only eliminated LT NO<sub>x</sub> but also promoted formation of greater quantities of adsorbed hydrocarbons.

### Introduction

With a growing demand to reduce fuel consumption, lean-burn and diesel engine vehicles will continue to comprise an increasing fraction of road-vehicles in the future. The regulation of NO<sub>x</sub> (NO+NO<sub>2</sub>) emissions from the transportation sector in the upcoming years will be more stringent and therefore it is urgently required to develop efficient and reliable NO<sub>x</sub> reduction aftertreatment systems for a wide variety of lean-burn or diesel engines. Selective catalytic reduction (SCR) of NO<sub>x</sub> with hydrocarbons (HC) has remained as one possible concept to catalytically reduce NO<sub>x</sub> emissions from lean-burn and diesel engine vehicles. For hydrocarbon-selective catalytic reduction (HC-SCR), Ag/Al<sub>2</sub>O<sub>3</sub> catalysts have been considered to have potential due to their lower cost, higher tolerance towards water vapor and sulfur<sup>1,2</sup> but also lower selectivity to N<sub>2</sub>O formation compared to PGM catalysts<sup>3</sup>.

However, it is important to mention that Ag/Al<sub>2</sub>O<sub>3</sub> exhibits poor NO<sub>x</sub> reduction activity in the lower temperature region. Below 400°C, the NO<sub>x</sub> reduction activity decreases abruptly which has been considered to be due to self-inhibition by adsorbed nitrates on the active sites of the catalyst<sup>4</sup>. It has been shown that addition of H<sub>2</sub> can drastically promote NO<sub>x</sub> reduction activity in the lower temperature region<sup>5</sup>. The so called “H<sub>2</sub>-effect” results in better NO<sub>x</sub> reduction activity and a wider temperature operating window. Nevertheless, the reaction mechanism of HC-SCR over Ag/Al<sub>2</sub>O<sub>3</sub> remains a challenging issue since it involves a number of reaction intermediates and surface species during the reaction. As a result, the mechanisms by which H<sub>2</sub> promotes NO<sub>x</sub> reduction with Ag/Al<sub>2</sub>O<sub>3</sub> are not entirely identified.

Generally, the reaction mechanism of HC-SCR over Ag/Al<sub>2</sub>O<sub>3</sub> is initiated by activation of NO<sub>x</sub> and HC. Activation of NO<sub>x</sub> is characterized by formation of surface NO<sub>x</sub> species mainly as nitrate and/or nitrite species. Subsequently, oxygen partially oxidizes hydrocarbons (HC activation) to form oxygenated HC surface species which react further with surface NO<sub>x</sub> species and eventually lead to the formation of N<sub>2</sub>. For this reason, surface NO<sub>x</sub> species have been suggested to be important intermediates and therefore it is important to understand their formation, stability, reactivity and possible inhibition effects to elucidate the mechanism of HC-SCR.

Temperature-programmed desorption (TPD) is a useful

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**Table 1** Composition of adsorption gases, space velocity and duration of adsorption steps in flow reactor experiments.

TPD type	Gas mixture (GM)	Adsorption gases <sup>a</sup>	2 wt.% Ag-Al <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
			Duration (min)	WHSV (h <sup>-1</sup> ) <sup>b</sup>	Duration (min)	WHSV (h <sup>-1</sup> ) <sup>b</sup>
NO oxidation	GM 1	500 ppm NO + 4 % O <sub>2</sub>	30	266	30	231
H <sub>2</sub> -assisted NO oxidation	GM 2	500 ppm NO + 4 % O <sub>2</sub> +0.1 % H <sub>2</sub>	30	266	30	231
NO <sub>2</sub> -O <sub>2</sub> adsorption	GM 3	150 ppm NO <sub>2</sub> + 4 % O <sub>2</sub>	120	620	180	231
C <sub>3</sub> H <sub>6</sub> -SCR	GM 4	500 ppm NO + 0.1 % C <sub>3</sub> H <sub>6</sub> + 4 % O <sub>2</sub>	30	266	-	-
H <sub>2</sub> -assisted C <sub>3</sub> H <sub>6</sub> SCR	GM 5	500 ppm NO + 0.1 % C <sub>3</sub> H <sub>6</sub> + 4 % O <sub>2</sub> + 0.1 % H <sub>2</sub>	30	266	-	-

<sup>a</sup> Ar was always used as carrier gas.

<sup>b</sup> Weight hourly space velocity (WHSV) is the ratio of mass flow rate and mass of catalyst material

technique to investigate the thermal stability of adsorbed species. TPD studies to investigate the stability of surface NO<sub>x</sub> species over Ag/Al<sub>2</sub>O<sub>3</sub> have been reported in the literature<sup>6-9</sup>. Following adsorption of NO and O<sub>2</sub> over Ag/Al<sub>2</sub>O<sub>3</sub>, two NO<sub>x</sub> desorption peaks at low temperature (250-340°C) and high temperature (435-539°C) have been reported<sup>6,9</sup>. Several attempts were made to identify the origin of these NO<sub>x</sub> desorption peaks. By combining TPD and IR spectroscopy, Kameoka et al.<sup>6</sup> found that the peaks originated from three types of surface nitrates i.e. bridging, bidentate and monodentate nitrates. From additional TPD studies<sup>7-9</sup>, it was pointed out that NO<sub>x</sub> desorption peaks at high temperature (~440°C<sup>7,8</sup> and 539°C<sup>9</sup>) resulted from surface nitrate decomposition.

It is interesting to note that H<sub>2</sub> may play a dual role in its interaction with nitrate species. On one hand, H<sub>2</sub> has been proposed to promote elimination of nitrates during H<sub>2</sub>-assisted HC-SCR<sup>10-16</sup>. On the other hand, it has also been shown that H<sub>2</sub> activates accumulation of nitrates on the surface, especially during NO oxidation<sup>8,10,17-19</sup>.

Elimination of surface nitrates from the active silver species by H<sub>2</sub> has been proposed as one probable key step in the “H<sub>2</sub>-effect” for low temperature HC-SCR<sup>10-16</sup>. H<sub>2</sub> has also been found to promote NO oxidation<sup>8,13,17,18,20</sup> and our previous study has simulated H<sub>2</sub>-assisted NO oxidation based on the main role of H<sub>2</sub> to eliminate poisonous surface nitrate species<sup>21</sup>. It is important to mention, however, that H<sub>2</sub> has been proposed to have several other roles in HC-SCR which have been discussed in the literature such as to facilitate modification of surface species and active Ag sites<sup>5,10,12,13,16,22,23</sup>.

Seemingly contradictory to hydrogen’s proposed role to eliminate nitrates during HC-SCR, in-situ FTIR studies have been widely presented in the literature showing that H<sub>2</sub> plays an important role to activate the accumulation of surface nitrates following exposure of the catalyst to a NO-O<sub>2</sub>-H<sub>2</sub> gas mixture<sup>10,17-19</sup>. Recently, Kim et al.<sup>23</sup> also suggested that the kinetic effects of H<sub>2</sub> was to promote formation of surface nitrate that later reacts with adsorbed HC. With the low silver loadings that are common for Ag/Al<sub>2</sub>O<sub>3</sub> catalysts, it is also reasonable to expect that alumina also facilitates adsorption of surface NO<sub>x</sub> species. In addition, the existence of both silver nitrate and aluminium nitrate and their interaction following NO<sub>x</sub> adsorption has been proposed<sup>8,11,24</sup>. Unfortunately, in-situ IR analysis indicates overlapping peaks for nitrates over Ag/Al<sub>2</sub>O<sub>3</sub> and bare Al<sub>2</sub>O<sub>3</sub> which makes it

difficult to discriminate between nitrates on the Al<sub>2</sub>O<sub>3</sub> support and silver particles<sup>17,25,26</sup>.

In the present work, a series of TPD studies of NO<sub>x</sub> were carried out over Ag-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> catalysts to quantify and characterize the stability of surface NO<sub>x</sub> species related to Ag-Al<sub>2</sub>O<sub>3</sub> as a HC-SCR catalyst. In addition, in-situ DRIFT spectroscopy experiments were also carried out to characterize formation of adsorbed NO<sub>x</sub> species. This study has also aimed to demonstrate the effect of H<sub>2</sub> to modify the quantities and position of surface NO<sub>x</sub> species. These effects will also be correlated to the activity of the catalyst for NO oxidation and C<sub>3</sub>H<sub>6</sub>-SCR to determine quantitatively to what extent H<sub>2</sub> removal of inhibiting nitrates may contribute to the so called “H<sub>2</sub>-effect”. An additional objective for studying surface NO<sub>x</sub> species was to examine whether these apparently contradictory roles for H<sub>2</sub>, discussed above, could be compatible. We have focused our work on the low temperature region 200-300°C as it is expected to be favorable for formation of surface NO<sub>x</sub> species and therefore most relevant to understand the H<sub>2</sub>-effect in modification of surface NO<sub>x</sub> species.

## Experimental method

### Catalyst preparation

Ag-Al<sub>2</sub>O<sub>3</sub> with 2 wt.% Ag loading on Al<sub>2</sub>O<sub>3</sub> was prepared by a freeze dried sol-gel method. The powder was then washcoated onto a cordierite monolith with a diameter of 2 cm. Ag-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> were washcoated onto 2 cm and 4 cm long cordierite monoliths respectively. Approximately 0.5 g of Ag-Al<sub>2</sub>O<sub>3</sub> and 1.5 g Al<sub>2</sub>O<sub>3</sub> was deposited onto the cordierite monoliths. The specific surface area of powders measured by N<sub>2</sub> sorption (BET Method) gave specific surface areas of 188 m<sup>2</sup>/g and 233 m<sup>2</sup>/g for Ag-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>, respectively. The details of methods for preparation and coating of monoliths were described elsewhere<sup>21,27</sup>.

### Flow reactor experiments

TPD experiments were performed in a horizontal quartz tube reactor 88 cm long with 2 cm diameter. The monolith sample was placed inside the reactor tube and thermocouples were used to measure both the monolith temperature and inlet gas temperatures. To minimize axial temperature gradients in the monolith sample, a number of blank monoliths (with total length

**Table 2** Composition of adsorption gases and duration of adsorption steps for in-situ DRIFT Spectroscopy

No.	Adsorption step	Adsorption gases	Duration (min.)
1.	NO Oxidation	1000 ppm NO + 8% O <sub>2</sub>	30
2.	H <sub>2</sub> -assisted NO Oxidation	1000 ppm NO + 8% O <sub>2</sub> + 0.2 % H <sub>2</sub>	30
3.	NO <sub>2</sub> -O <sub>2</sub> adsorption	300 ppm NO <sub>2</sub> + 8% O <sub>2</sub>	60
4.	C <sub>3</sub> H <sub>6</sub> -SCR	1000 ppm NO + 8% O <sub>2</sub> + 2000 ppm C <sub>3</sub> H <sub>6</sub>	30
5.	H <sub>2</sub> -assisted C <sub>3</sub> H <sub>6</sub> -SCR	1000 ppm NO + 8% O <sub>2</sub> + 2000 ppm C <sub>3</sub> H <sub>6</sub> + 0.2% H <sub>2</sub>	30

of 14 cm) were placed to fill the empty space between the monolith and outlet end of the reactor. A test with only blank monoliths indicated that these blank monoliths were inert. To provide heat to the reactor, a spiral-shaped electrical heater was used around the reactor tube. A number of quartz wool layers were used to bundle the reactor tube in order to minimize heat loss.

Several mass flow controllers (Bronkhorst) were used to supply gas flow to the reactor tube. Ar was used as a carrier gas in all experiments. The outlet flow from the reactor was sent to gas analyzers. A FTIR MKS 2000 was utilized to measure the majority of gas outlet component concentrations including NO, NO<sub>2</sub>, N<sub>2</sub>O, CO, C<sub>3</sub>H<sub>6</sub>, and NH<sub>3</sub> in ppm level. In addition, a Hiden HPR 20 quadrupole mass spectrometer (MS) was employed to sample a small fraction of the outlet stream to detect variations in concentrations of some components from the following mass to charge (m/z) ratios: 2 (H<sub>2</sub>), 16 and 32 (O<sub>2</sub>), 28 (N<sub>2</sub> and CO), and 44 (CO<sub>2</sub>). To present O<sub>2</sub> measurement results, m/z 16 was selected from MS measurement.

Temperature-programmed desorption experiments (TPD) were initiated by pretreatment of the catalyst with 8% O<sub>2</sub> for 20 minutes at 550°C. Subsequently, the catalyst temperature was cooled down to a targeted adsorption temperature: 200, 250 or 300°C. An adsorption gas mixture was introduced for a certain time as depicted in Table 1. After the adsorption step, feed of adsorption species were terminated and a flow of only Ar was maintained. The catalyst temperature was then kept constant at the adsorption temperature for 5 minutes to flush away any loosely bound surface species. Subsequently, the catalyst temperature was either maintained or decreased to 200°C during a period of 30 min in Ar flow to allow further stabilization of the adsorbed species. The desorption step was performed by increasing the inlet gas temperature from 200 to 550°C at a rate of 40°C/min in Ar flow. Due to temperature gradients between measured inlet and catalyst temperatures, the maximum catalyst temperature reached varied between 530 to 545°C. The catalyst temperature was the temperature used to identify the desorption profile and is therefore presented in all TPD results below.

During adsorption with C<sub>3</sub>H<sub>6</sub>-SCR conditions (GM 4 in Table 1), H<sub>2</sub>-assisted C<sub>3</sub>H<sub>6</sub>-SCR (GM 5 in Table 1) as well as the following desorption steps, it was found that formation of N<sub>2</sub>O according to the FTIR analysis was negligible. Therefore, m/z 44 from MS measurement could be used as a reliable indicator of CO<sub>2</sub> concentration with calibration. These MS measurements of CO<sub>2</sub> concentration agreed quantitatively with average FTIR measurements but were found to be far less noisy and are thus reported here.

Total flow rates of gases during flow reactor experiments were

varied between 1500-3500 mLn/min. As a result, different weight hourly space velocities (WHSV) were used for the Ag-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> catalysts based on the masses of catalyst material deposited on monoliths as shown in Table 1. It is thus noteworthy that the quantities of adsorbed species cannot be compared directly by merely inspecting the level of gas concentrations from TPD results over Ag-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>. A lower WHSV was usually used for the Al<sub>2</sub>O<sub>3</sub> catalyst because it was expected that the quantities of adsorbed species would be lower compared to Ag-Al<sub>2</sub>O<sub>3</sub> and thus there would be a risk that the desorbed quantities may be undetectable during the TPD experiments. Nevertheless, correct comparisons could be made since the flow reactor experimental results were integrated to calculate the quantities of adsorbed/desorbed NO<sub>x</sub> species per mass of catalyst materials.

### In-situ DRIFT Spectroscopy

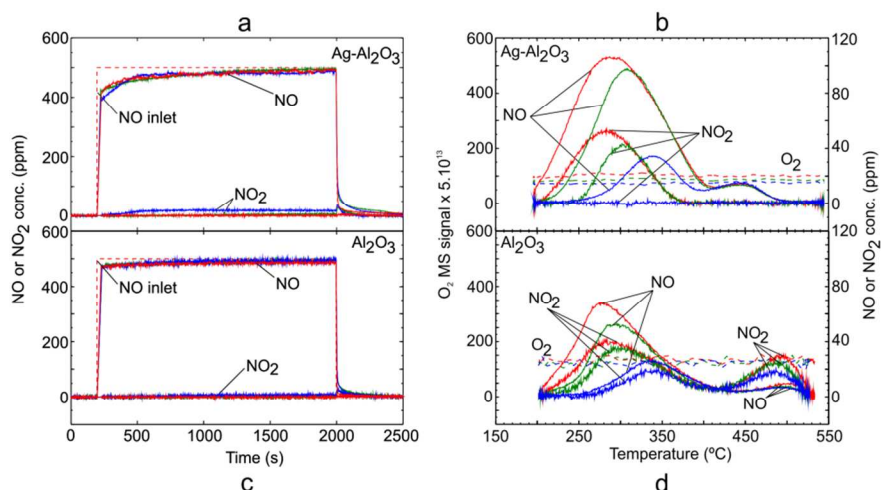
The DRIFT instrument used in this work was a Bio Rad FTS6000 Spectrometer. The sample powder of 2 wt.% Ag-Al<sub>2</sub>O<sub>3</sub> was placed in a sample holder (supported by a metallic grid) of a high temperature Harrick Praying Mantis cell coated with Silcolloy® 1000 and equipped with KBr windows. The gases were supplied by a number of mass flow controllers (Bronkhorst Hi-Tech). The total flow used was 100 mLn/min with Ar as the inert balance. The weight of sample powder was ca. 90 mg. To regulate temperature, the DRIFT cell was equipped with a Eurotherm heating system and water cooling system. In addition, a K-type thermocouple was placed near the sample holder to indicate the bed temperature.

The DRIFT experiments were conducted following a similar TPD protocol that consisted of adsorption and desorption steps with temperature ramps. Prior to each experiment, the sample was pretreated with 8% O<sub>2</sub> at 500°C for 30 min. Subsequently, the cell temperature was decreased to 200°C in inert gas flow. Here, background spectra were collected prior to each adsorption step by accumulating 60 scans with a resolution of 1 cm<sup>-1</sup>. The accumulation of IR spectra was initiated 2 min before the adsorption step by collecting 6 scans/min with a resolution of 1 cm<sup>-1</sup>. Table 2 shows the details of the adsorption step conditions. After the adsorption step, the cell temperature was kept constant at 200°C for 10 min to stabilize adsorbed species in Ar flow. Subsequently, the cell temperature was raised to 500°C with a ramping rate of 20°C/min. The IR spectra were collected continuously during adsorption and desorption steps.

## Results

### TPD following NO oxidation

In order to investigate formation of surface NO<sub>x</sub> species,



**Fig. 1** TPD following NO oxidation over Ag-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> showing the adsorption steps (a,c) and desorption profiles (b,d) at adsorption temperature 200 (red), 250 (green) and 300°C (blue). Adsorption condition GM1 as displayed in Table 1 was used.

adsorption conditions with NO-O<sub>2</sub> gas mixture (GM 1) was carried out over Ag-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>. Figure 1 shows the NO<sub>x</sub> uptake during the adsorption step and TPD profile over Ag-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>. The amount of NO<sub>x</sub> adsorbed and desorbed was calculated by integrating the NO<sub>x</sub> curves over these catalysts and normalized to the mass of catalyst. The results from integration are displayed in Table 3.

As seen from Fig. 1 and Table 3, the quantities of NO<sub>x</sub> adsorbed decreased with increasing adsorption temperature. It was found that the duration of adsorption was in all cases sufficiently long to reach steady state reaction conditions and thus the catalyst was saturated with adsorbed species for each set of conditions. Conversion of NO to NO<sub>2</sub> during the adsorption step over Ag-Al<sub>2</sub>O<sub>3</sub> (Fig. 1a) was low and negligible at 200 and 250°C. At 300°C, there was a detectable conversion of NO to NO<sub>2</sub> of about 4%. Following the switch from the adsorption gas mixture to only Ar flow, there was desorption of loosely bound surface NO<sub>x</sub> species.

Figure 1b shows the desorption profiles of NO<sub>x</sub> over Ag-Al<sub>2</sub>O<sub>3</sub>. During the temperature ramp for Ag-Al<sub>2</sub>O<sub>3</sub>, two NO<sub>x</sub> desorption peaks were observed i.e. a low temperature (LT) peak at 277-340°C and high temperature (HT) peak at ca. 440°C. It is

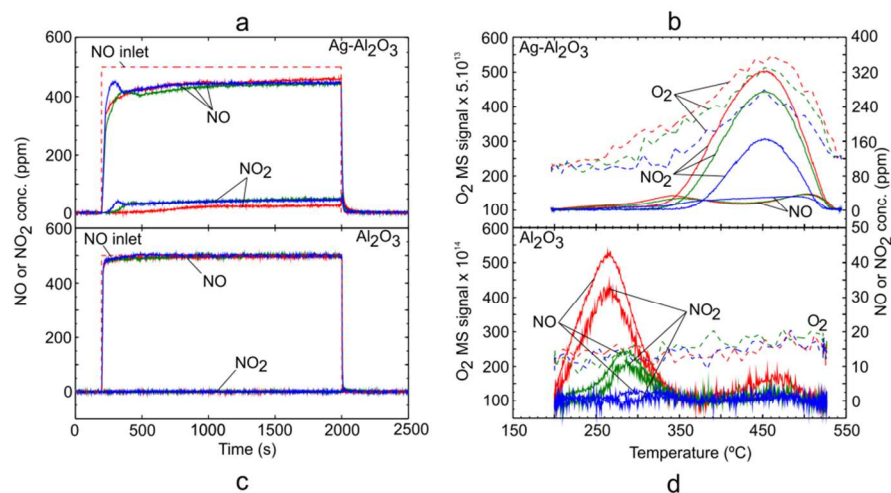
noteworthy that the LT peaks were skewed to higher temperatures with increasing adsorption temperature. The major NO<sub>x</sub> components desorbed were NO at both LT and HT peaks whereas NO<sub>2</sub> was only observed at the LT peak following adsorption at 200 and 250°C. No O<sub>2</sub> release was observed during the desorption steps following all adsorption temperatures.

In order to investigate the formation of surface NO<sub>x</sub> species over Al<sub>2</sub>O<sub>3</sub>, similar TPD studies following NO oxidation were conducted on Al<sub>2</sub>O<sub>3</sub> (Fig. 1c and 1d). As seen from Fig. 1c, the NO oxidation conversion to NO<sub>2</sub> was negligible and at the highest temperature 300°C, only ca. 8 ppm of NO<sub>2</sub> (~1.6 % conversion) was observed. Thus, it can be said that both Ag-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> could be considered as a relatively poor NO oxidation catalysts below 300°C. From the desorption profile (Fig. 1d), two desorption peaks were observed, similar to that for the Ag-Al<sub>2</sub>O<sub>3</sub> catalyst. The characteristics and location of the LT peak resembled that for Ag-Al<sub>2</sub>O<sub>3</sub>. However, the HT peak over Al<sub>2</sub>O<sub>3</sub> was shifted to a higher temperature of 486°C. The major gas desorbed at the LT peak was NO followed by a slightly lower amount of NO<sub>2</sub>. Whereas, decomposition of surface NO<sub>x</sub> species at the HT peak gave mostly NO<sub>2</sub>. Similar to Ag-Al<sub>2</sub>O<sub>3</sub>, no

**Table 3** Quantities of NO<sub>x</sub> adsorbed and desorbed over Ag-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>.

Adsorption conditions	Ag-Al <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
	NO <sub>x</sub> adsorbed (μmol/g)	NO <sub>x</sub> desorbed (μmol/g)	NO <sub>x</sub> adsorbed (μmol/g)	NO <sub>x</sub> desorbed (μmol/g)
TPD NO-O <sub>2</sub>				
200 °C	111.4	110.7	61.9	59.6
250°C	98.2	98.1	57.9	57.7
300°C	59.3	58.7	41.5	40.9
TPD NO-O <sub>2</sub> -H <sub>2</sub>				
200 °C	189.6	188.8	31.3	28.7
250°C	153.5	150.8	17.8	14.0
300°C	103.7	100.4	8.8	6.8
TPD NO <sub>2</sub> -O <sub>2</sub>				
200 °C	450.8	448.9	357.6	356.6
250°C	337.9	335.4	282.3	281.2
300°C	245.7	242.4	212.6	210.8

50



**Fig. 2** TPD following  $H_2$ -assisted NO oxidation over  $Ag-Al_2O_3$  and  $Al_2O_3$  showing the adsorption steps (a,c) and desorption profiles (b,d) at adsorption temperature 200 (red), 250 (green) and 300°C (blue). Adsorption condition GM2 as displayed in Table 1 was used.

desorption of  $O_2$  was observed during temperature ramps following all adsorption temperatures.

#### TPD following $H_2$ -assisted NO oxidation

Addition of  $H_2$  has been shown to promote NO oxidation activity over  $Ag-Al_2O_3$  catalysts<sup>5, 8, 13, 17, 18, 20, 21</sup>. TPD studies using a NO- $O_2$ - $H_2$  adsorption gas mixture (GM 2) were carried out over  $Ag-Al_2O_3$  and  $Al_2O_3$ . Figure 2 shows the  $NO_x$  uptake and TPD profile for the NO- $O_2$ - $H_2$  system over  $Ag-Al_2O_3$  and  $Al_2O_3$  catalysts. The duration of adsorption was in all cases sufficiently long to reach steady state reaction conditions. As shown in Fig. 2a, NO oxidation conversion to  $NO_2$  was detected and increased from 5% at 200°C to 10% at 250 and 300°C during the adsorption step with  $Ag-Al_2O_3$ . In addition, formation of  $N_2O$  and  $NH_3$  were negligible at below 5 ppm and 1 ppm (not shown), respectively. Likewise,  $NO_x$  conversion was not observed.

During the temperature ramp with  $Ag-Al_2O_3$  (Fig. 2b), the desorption peak of  $NO_2$  at ca.450°C was clearly observed which can be assigned as the HT peak as observed from NO- $O_2$  TPD (Fig. 1b). Desorption of  $O_2$  was also observable and coincided well with the  $NO_2$  peak. In addition, desorption of low concentrations of NO were observed at ca. 340-350°C and 505°C. It is noteworthy that  $H_2$  desorption was not observed at all temperatures.

It can be noted that along with higher activity for NO oxidation in the presence of  $H_2$ , the LT peak which was observed in the NO- $O_2$  system was significantly suppressed and shifted towards the HT peak. The shift was also accompanied by higher total quantities of  $NO_x$  adsorbed and desorbed as displayed in Table 3. The results from the TPD study with  $Al_2O_3$  with adsorption gases GM 2 are shown in Fig. 2c and 2d. During the adsorption step (Fig. 2c), NO conversion to  $NO_2$  was negligible at all temperatures. Therefore, it could be concluded that  $H_2$  did not promote NO oxidation to  $NO_2$ , but instead it acted as a reductant which also decreased the amount of  $NO_x$  adsorbed compared to the NO- $O_2$  system over  $Al_2O_3$  (see Fig. 1c and Table 3).

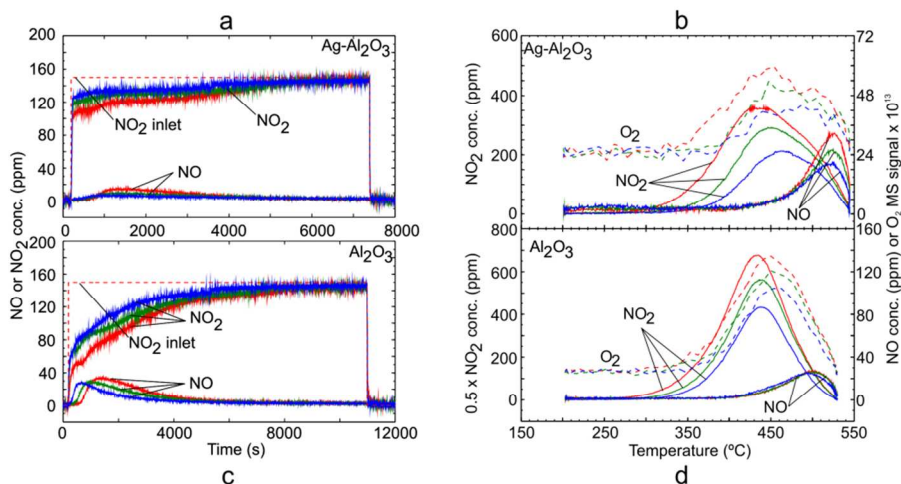
During the temperature ramp with  $Al_2O_3$  (Fig. 2d), the LT and HT desorption peaks were observable for adsorption temperatures 200 and 250°C. The LT peak (at 270-280°) was markedly higher

than the HT peak (at ca.460°). The LT peak consisted of NO and  $NO_2$  where the quantities of NO were slightly higher than  $NO_2$ . Decomposition of HT species gave only desorption of  $NO_2$ . At an adsorption temperature of 300°C, the desorption peaks of  $NO_x$  were at trace levels. In addition, no desorption of  $O_2$  was observed following all studied adsorption temperatures.

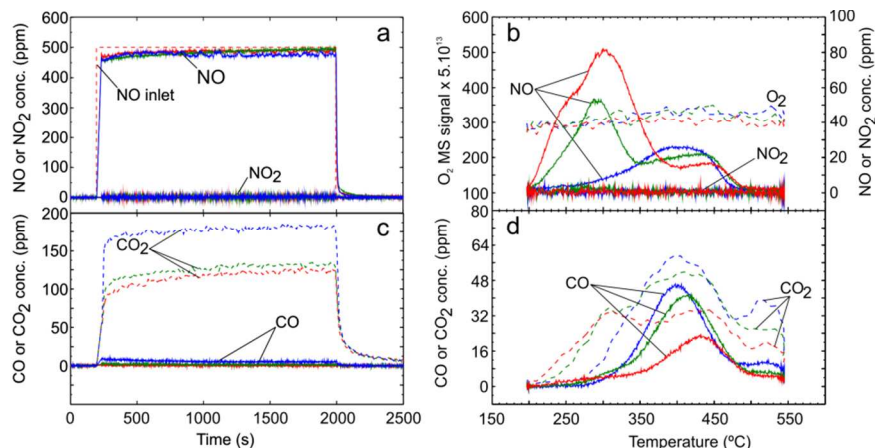
#### TPD following $NO_2$ adsorption

In order to investigate the adsorption of  $NO_2$  on  $Ag-Al_2O_3$  and  $Al_2O_3$  at conditions comparable to those for NO oxidation above, i.e. with excess  $O_2$  present, TPD experiments following exposure to gas mixture GM 3 were conducted. Figure 3 shows the  $NO_x$  uptake and  $NO_x$  desorption profiles for both catalysts. As seen from the adsorption step over  $Ag-Al_2O_3$  (Fig. 3a), a temporary formation of NO could be detected during  $NO_2$  adsorption. The quantities of  $NO_x$  uptake decreased with higher adsorption temperature as also displayed in Table 3. The  $NO_2$ - $O_2$  system took much longer time to reach stable outlet  $NO_x$  signals during the adsorption steps compared to the NO- $O_2$  system due to the larger formation of surface  $NO_x$  species on the catalysts as evident from Table 3. During the temperature ramp over  $Ag-Al_2O_3$  (Fig. 3b), a substantial release of  $NO_2$  was observed that peaked at 440-460°C. A minor desorption of NO was also detected at higher temperature ~525°C. A broad release of  $O_2$  was observed reaching a peak at ~450-475°C.

A similar TPD study with GM 3 was also conducted over the  $Al_2O_3$  sample. Figure 3c shows the  $NO_x$  uptake over the  $Al_2O_3$  catalyst and it gave a profile similar to that for the  $Ag-Al_2O_3$  catalyst. Along with adsorption of  $NO_2$ , temporary NO formation was also observed and reached a peak of ca. 35 ppm (adsorption temperature 200°C) of NO followed by a continuous decrease to 500°C. Similar to  $Ag-Al_2O_3$ , a broad  $O_2$  peak was observed with a peak at ~450°C. In general, one can notice that the desorption profiles of  $NO_x$  over  $Ag-Al_2O_3$  and  $Al_2O_3$  after  $NO_2$  adsorption were similar. Comparing the quantities of  $NO_x$ , it can be seen from Table 3 that the amount of  $NO_x$  adsorbed on  $Ag-Al_2O_3$  is comparable to  $Al_2O_3$  but somewhat greater on the  $Ag-Al_2O_3$ . It should be noted that in this case since the WHSV used for  $Ag-Al_2O_3$  (620  $h^{-1}$ ) was much higher than that for  $Al_2O_3$  (231  $h^{-1}$ ), the



**Fig. 3** TPD following  $\text{NO}_2$  adsorption over  $\text{Ag-Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  showing the adsorption steps (a,c) and desorption profiles (b,d) at adsorption temperature 200 (red), 250 (green) and 300°C (blue). Adsorption condition GM3 as displayed in Table 1 was used.



**Fig. 4** TPD following  $\text{C}_3\text{H}_6$ -SCR over  $\text{Ag-Al}_2\text{O}_3$  showing adsorption (a) and desorption (b) of  $\text{NO}_x$ , adsorption (c) and desorption (d) of  $\text{CO}_x$ . Adsorption condition GM4 as displayed in Table 1 was used at adsorption temperatures 200 (red), 250 (green) and 300°C (blue).

quantities of  $\text{NO}_x$  adsorbed cannot be compared directly from Fig. 3a and 3c.

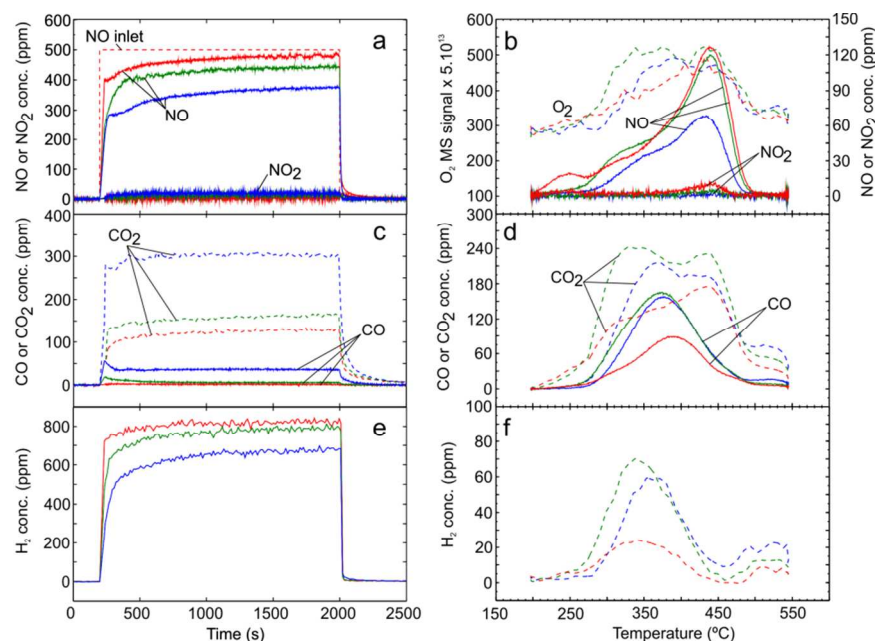
#### TPD following $\text{C}_3\text{H}_6$ -SCR and $\text{H}_2$ -assisted $\text{C}_3\text{H}_6$ -SCR

Further TPD studies were conducted to investigate the quantities and nature of adsorbed  $\text{NO}_x$  and  $\text{CO}_x$  species during  $\text{C}_3\text{H}_6$ -SCR and  $\text{H}_2$ -assisted  $\text{C}_3\text{H}_6$ -SCR over the  $\text{Ag-Al}_2\text{O}_3$  catalyst. Figure 4 presents TPD results following exposure to the  $\text{C}_3\text{H}_6$ -SCR gas mixture (GM 4) in the absence of  $\text{H}_2$  where panels 4a to 4d show the  $\text{NO}_x$  uptake, desorption profile of  $\text{NO}_x$ ,  $\text{CO}_x$  formation during adsorption and the desorption profile of  $\text{CO}_x$  respectively.

During the adsorption step (Fig. 4a), the NO signal increased rapidly and  $\text{NO}_2$  yield was found to be negligible. Formation of  $\text{N}_2\text{O}$  (not shown) was negligible at below 5 ppm during  $\text{C}_3\text{H}_6$ -SCR and also later during  $\text{H}_2$ -assisted  $\text{C}_3\text{H}_6$ -SCR. Similarly, formation of  $\text{NH}_3$  (not shown) was negligible at below 1 ppm both during  $\text{C}_3\text{H}_6$ -SCR and  $\text{H}_2$ -assisted  $\text{C}_3\text{H}_6$ -SCR. The  $\text{NO}_x$  conversion during the adsorption step was negligible at less than 250°C and increased to ~6% at 300°C. Furthermore,  $\text{C}_3\text{H}_6$  conversion to  $\text{CO}_2$  and CO was also observed during the adsorption step for  $\text{C}_3\text{H}_6$ -SCR (Fig. 4c).

During the temperature ramp (Fig. 4b), two remarkable  $\text{NO}_x$  peaks could be observed at ca. 290°C (LT) and 420°C (HT). It should be noted that following adsorption at 200°C a shoulder on the NO peak at ca. 235°C could be seen. The LT  $\text{NO}_x$  desorption quantity decreased with higher adsorption temperature and became markedly suppressed at the adsorption temperature of 300°C. In addition, it could be seen that almost no  $\text{O}_2$  desorption was detected during desorption step. From Fig. 4d, the CO desorption peak was observed between 405 to 426°C while the  $\text{CO}_2$  desorption peak was broad with the same rise and decline as the CO profile.

In order to investigate the influence of  $\text{H}_2$  on  $\text{C}_3\text{H}_6$ -SCR, 0.1%  $\text{H}_2$  was added in the adsorption step with gas mixture GM 5. Figures 5a to 5f showing the  $\text{NO}_x$  uptake, desorption profile of  $\text{NO}_x$ ,  $\text{CO}_x$  formation during adsorption, desorption profile of  $\text{CO}_x$ ,  $\text{H}_2$  profile during adsorption and desorption profile of  $\text{H}_2$  respectively. During the adsorption step (Fig. 5a), NO consumption and  $\text{NO}_2$  formation were observed and increased with higher adsorption temperature. An  $\text{NO}_2$  yield of up to 20 ppm was observed at adsorption temperature 300°C. Similarly, higher formation of CO and  $\text{CO}_2$  were observed in comparison



**Fig. 5** TPD following  $H_2$ -assisted  $C_3H_6$ -SCR over  $Ag-Al_2O_3$  showing adsorption (a) and desorption (b) of  $NO_x$ , adsorption (c) and desorption (d) of  $CO_x$ . Adsorption condition GM5 as displayed in Table 1 was used at adsorption temperatures 200 (red), 250 (green) and 300°C (blue).

5

with the absence of  $H_2$  (comparing Fig. 5c and 4c) indicating a higher conversion of  $C_3H_6$ . Consumption of  $H_2$  during the adsorption step (Fig. 5e) markedly increased with higher adsorption temperature. As expected, addition of  $H_2$  gave higher  $NO_x$  conversion than in the absence of  $H_2$  and a  $NO_x$  conversion up to 23% was observed at 300°C. During the desorption step (Fig. 5b), a small peak of  $NO$  at 240°C and a broad desorption peak reaching a maximum at ~440°C were observed whereas  $NO_2$  desorption was negligible. These  $NO$  peaks decreased with higher adsorption temperature. The quantities of desorbed  $NO_x$  in the presence of  $H_2$  were higher than in the absence of  $H_2$  as shown in Table 4. In addition, it could be observed that a broad  $O_2$  desorption was clearly detected accompanying  $NO_x$  desorption.

From the desorption profile of  $CO$  and  $CO_2$  (Fig. 5d), one can see that a  $CO$  peak was observed at ca. 375°C which is at lower temperature compared to the one in the absence of  $H_2$ . Furthermore, the concentration of  $CO_x$  released was much higher than in the absence of  $H_2$  consistent with the higher conversion of  $C_3H_6$  obtained with addition of  $H_2$ . As seen from Fig. 5d and 4d, it can be noted that  $CO_x$  desorption both in the case of  $C_3H_6$ -SCR with and without  $H_2$  addition does not monotonically decrease with increasing adsorption temperature as was the case with  $NO_x$ . Similarly, the desorption profile of  $H_2$  approximately coincided with the  $CO$  desorption as shown in Fig. 5f.

**Table 4** Quantities of  $NO_x$  desorbed over  $Ag-Al_2O_3$  after  $C_3H_6$ -SCR and  $H_2$ -assisted  $C_3H_6$ -SCR

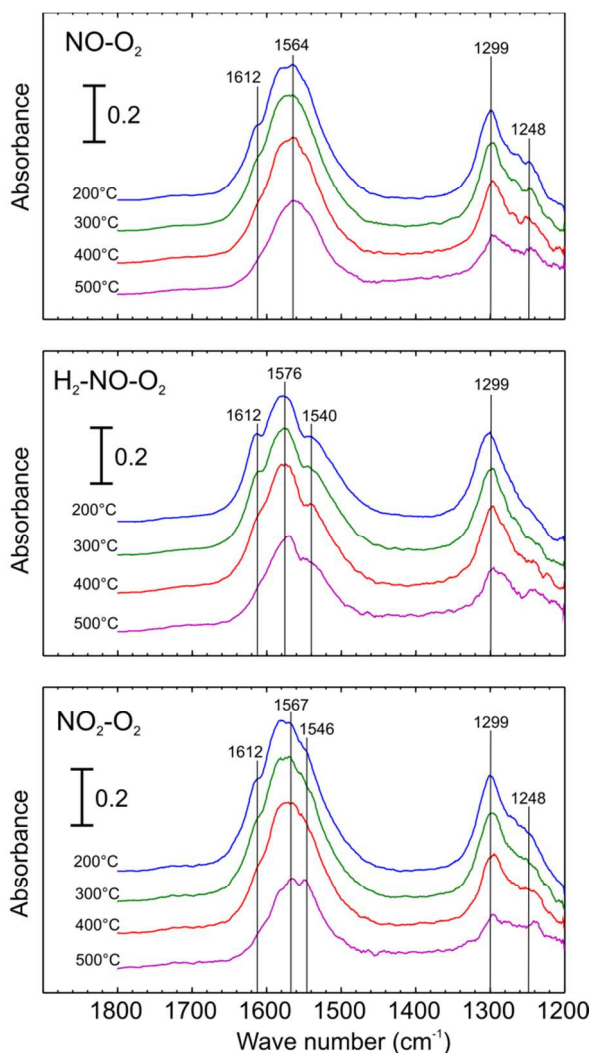
Adsorption Conditions	$C_3H_6$ -SCR $NO_x$ desorbed ( $\mu\text{mol/g}$ )	$H_2$ -assisted $C_3H_6$ -SCR $NO_x$ desorbed ( $\mu\text{mol/g}$ )
200 °C	70.7	91.4
250°C	53.5	69.3
300°C	35.4	50.3

#### Identification and stability of adsorbed surface $NO_x$ species from in-situ DRIFT

DRIFT spectroscopy was used to investigate types of adsorbed surface  $NO_x$  species over  $Ag-Al_2O_3$ . Since the focus was to identify surface  $NO_x$  species, only DRIFT spectra within the range of 1200-1800  $\text{cm}^{-1}$  are presented. Here, adsorption steps were conducted at 200°C to obtain a high quantity of  $NO_x$  adsorbed species. Figure 6 shows the evolution of IR spectra ensuing the increase of cell temperature during the desorption steps. Here, the adsorption steps were  $NO$  oxidation,  $H_2$ -assisted  $NO$  oxidation and  $NO_2$ - $O_2$  adsorption (conditions 1-3 respectively in table 2). As seen from the top panel of figure 6 at 200°C, adsorption of  $NO$ - $O_2$  resulted in the appearances of peaks at 1299 and a broad peak at 1564  $\text{cm}^{-1}$ . Further, a small peak or shoulder at 1248 and 1612  $\text{cm}^{-1}$  were also seen. When  $H_2$  was added with  $NO$  and  $O_2$  (middle panel), several peaks were observed: a notable peak at 1299, a broad peak at 1576 and shoulders at 1612 and 1540  $\text{cm}^{-1}$ . It is important to mention that the shoulder peak at 1248  $\text{cm}^{-1}$ , clearly evident for the  $NO$ - $O_2$  system, declined in the presence of  $H_2$ . When the catalyst was exposed to  $NO_2$ - $O_2$  adsorption (bottom panel), IR spectra with vibration bands at 1248, 1299, shoulder at 1546, a broad peak at ca. 1567 and shoulder at 1612  $\text{cm}^{-1}$  were observed.

Possible structures of adsorbed nitrate species namely monodentate nitrate, bidentate nitrate and bridging nitrate are shown in scheme 1 and peak assignments were mainly taken from our group's publications<sup>24, 28</sup>. The vibration band at 1248  $\text{cm}^{-1}$  can be assigned to bidentate nitrate as reported in literature<sup>10, 28</sup>. The peak at 1299 is also attributable to bidentate nitrate that was reported by literature at 1298, 1300 and 1304  $\text{cm}^{-1}$ <sup>28, 29</sup>. In the higher wavenumber regions (approximately between 1540-1615  $\text{cm}^{-1}$ ), broad peaks at 1564 and 1576  $\text{cm}^{-1}$  were observed resulting

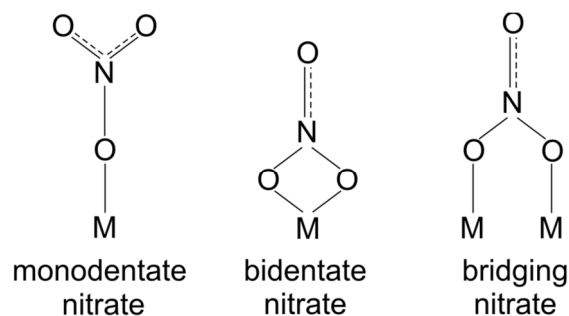




**Fig. 6** DRIFT Spectra of adsorbed species during temperature ramp and following adsorption with NO oxidation conditions (top), H<sub>2</sub>-assisted NO Oxidation conditions (centre) and NO<sub>2</sub>-O<sub>2</sub> adsorption (bottom) over 2 wt.% Ag-Al<sub>2</sub>O<sub>3</sub> at 200°C. Adsorption conditions are displayed in Table 2.

from the overlap of monodentate nitrate (1530-1546, 1558-1564 cm<sup>-1</sup>)<sup>24</sup> and bidentate nitrate (1570-1590 cm<sup>-1</sup>)<sup>24</sup>. In addition, the shoulder peaks observed at 1612 cm<sup>-1</sup> may be ascribed to the vibration of bridging nitrate that has been reported at 1614 cm<sup>-1</sup><sup>24, 25, 28</sup>.

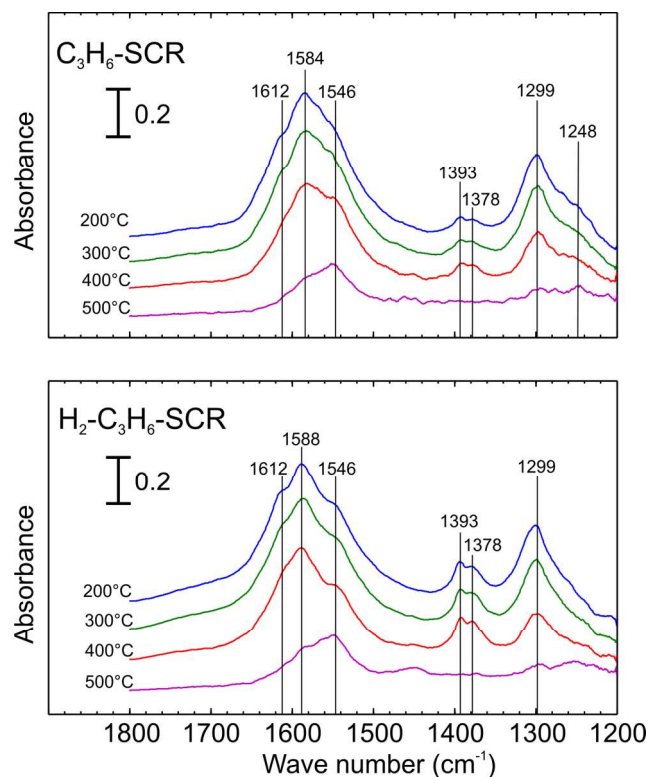
In order to investigate the thermal stability of adsorbed NO<sub>x</sub> species, the cell temperature was increased to 500°C in Ar flow. Figure 6 presents a number of IR spectra at different temperatures during the temperature ramp. As seen here, the intensity of the bridging nitrates (1612 cm<sup>-1</sup>) readily disappeared in all cases. Further, it can be observed that the subsequent peak that decreased abruptly was that of the bidentate nitrate. The broad peak at 1564 cm<sup>-1</sup> (top panel) and 1576 cm<sup>-1</sup> (middle and bottom panel) tended to shift to the lower wavenumbers resulting from a decrease in bidentate nitrates, indicating peak separation of bidentate and monodentate nitrates. Comparing the intensity of the monodentate nitrate band (1540 or 1546 cm<sup>-1</sup>), it is interesting to note that its presence is more prevalent in the case of H<sub>2</sub>-assisted NO oxidation (middle panel) and NO<sub>2</sub>-O<sub>2</sub> adsorption (bottom panel) compared to the case of NO-O<sub>2</sub> adsorption (top



**Scheme 1.** Possible structures of surface nitrate species (M=metal ion). Adapted from<sup>25</sup> and references therein.

panel). As seen during the temperature increase here, the intensity of monodentate nitrates are apparently the most stable among nitrate species.

Further in-situ DRIFT experiments were carried out to investigate the stability of adsorbed NO<sub>x</sub> species following adsorption with C<sub>3</sub>H<sub>6</sub>-SCR and H<sub>2</sub>-assisted C<sub>3</sub>H<sub>6</sub>-SCR conditions. Figure 7 presents the evolution of the DRIFT spectra during the temperature ramp following adsorption with C<sub>3</sub>H<sub>6</sub>-SCR and H<sub>2</sub>-assisted C<sub>3</sub>H<sub>6</sub>-SCR conditions. As seen from the top panel of figure 7 after adsorption from C<sub>3</sub>H<sub>6</sub>-SCR (indicated at 200°C), vibration bands assignable to monodentate nitrate at 1546 cm<sup>-1</sup> were observed. Strong vibration bands at 1299 and a broad peak at 1584 as well as shoulder at 1248 cm<sup>-1</sup>, ascribable to bidentate nitrate<sup>28</sup> were apparent. A shoulder peak at 1612 cm<sup>-1</sup>, assignable to bridging nitrate, was also detected as in previous cases. In addition, small bands were observed at 1393 and 1378 cm<sup>-1</sup> that may be ascribed to formate<sup>28</sup> or acetate<sup>29</sup> species and thus



**Fig. 7** DRIFT Spectra of adsorbed species during temperature ramp and following adsorption with C<sub>3</sub>H<sub>6</sub>-SCR (top) and H<sub>2</sub>-assisted C<sub>3</sub>H<sub>6</sub>-SCR conditions (bottom) over 2 wt.% Ag-Al<sub>2</sub>O<sub>3</sub> at 200°C. Adsorption conditions are displayed in Table 2.

unrelated to the vibration of surface NO<sub>x</sub> species.

When H<sub>2</sub> was added (lower panel of figure 7 at 200<sup>o</sup>C), similar IR spectra were obtained as in the case of C<sub>3</sub>H<sub>6</sub>-SCR adsorption conditions. In comparison to the case of C<sub>3</sub>H<sub>6</sub>-SCR conditions, it can be seen that the shoulder peak at 1248 cm<sup>-1</sup> had lower relative intensity. In contrast, the vibration band at 1546 cm<sup>-1</sup> had a higher relative intensity. Similar to C<sub>3</sub>H<sub>6</sub>-SCR, broad peaks at 1299 and 1588 cm<sup>-1</sup>, assignable to bidentate nitrates, were outstanding. Also a peak at 1612 cm<sup>-1</sup>, assignable to bridging nitrate, was also observable. Finally, peaks at 1393 and 1379 cm<sup>-1</sup> were observed with higher intensity for H<sub>2</sub>-assisted C<sub>3</sub>H<sub>6</sub>-SCR, attributed to acetate/formate species.

When the cell temperature was increased, as shown in figure 7, the bridging nitrates readily disappeared followed by a rapid decrease in bidentate nitrates at both 1588 and 1299 cm<sup>-1</sup>. At the highest temperature (500<sup>o</sup>C), again the vibration band assigned to monodentate nitrate (1546 cm<sup>-1</sup>) was still observable showing its strong stability at high temperature. It is noticeable that the acetate/formate species also have rather strong stability with temperature (lower panel of figure 7), having disappeared finally at 500<sup>o</sup>C.

## Discussion

### Formation of adsorbed NO<sub>x</sub> species from NO oxidation

From the results of TPD following NO-O<sub>2</sub> exposure over Ag-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>, the NO<sub>x</sub> desorption profile over both catalysts was similar showing two desorption peaks; one at low temperature referred to as the LT peak (a major peak) and one at high temperature referred to as the HT peak (a minor peak). The increase in NO oxidation conversion with increase in temperature was accompanied by a decrease in the LT NO<sub>x</sub> desorption peak. These NO<sub>x</sub> desorption peaks, can then be considered to originate from the decomposition of two types of surface NO<sub>x</sub> species: a less thermally stable LT surface NO<sub>x</sub> species and more stable HT surface NO<sub>x</sub> species.

From DRIFT results, the thermal stability of nitrate species were found to be in the order of bridging < bidentate < monodentate nitrate and therefore it is reasonable to regard the LT desorption peak to primarily originate from the decomposition of bidentate and bridging nitrate species, as in accordance with an earlier report<sup>6</sup>. In the presence of H<sub>2</sub> in the feed, it is apparent that the formation of the bidentate nitrate at 1248 cm<sup>-1</sup> was less pronounced. This result is in agreement with Shibata et al.<sup>10</sup> who reported minimal formation of a similar peak for H<sub>2</sub>-assisted C<sub>3</sub>H<sub>8</sub>-SCR. We therefore suggest that the vibration of bidentate nitrate at 1248 cm<sup>-1</sup> can also be associated with the LT desorption peak.

Klacar et al.<sup>30</sup> performed Density Functional Theory (DFT) calculations of NO<sub>x</sub> adsorption over oxidized silver. They found that adsorption of NO and NO<sub>2</sub> over oxidized silver yielded formation of nitrate species, especially on well-dispersed silver clusters (size of clusters 4-8 atoms) indicating that surface NO<sub>x</sub> species borrow O atoms from the Ag to form mainly bridging nitrates. Additionally, similar TPD profiles following NO-O<sub>2</sub> adsorption were observed for Ag-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> and hence a part of these surface NO<sub>x</sub> species were also on Al<sub>2</sub>O<sub>3</sub>. A similar phenomenon of surface nitrate formation by loaning O atoms

over Al<sub>2</sub>O<sub>3</sub> can also be speculated, as has been shown by Zhang et al.<sup>25</sup>. As seen from Fig. 1b and 1d, when the temperature was increased, the LT peak consisted of more NO than NO<sub>2</sub> and it was not accompanied by O<sub>2</sub> desorption. This observed ratio of desorbed atomic nitrogen to oxygen indicates that the decomposition of nitrate species giving the LT peak should leave borrowed O atoms on Ag and Al<sub>2</sub>O<sub>3</sub>.

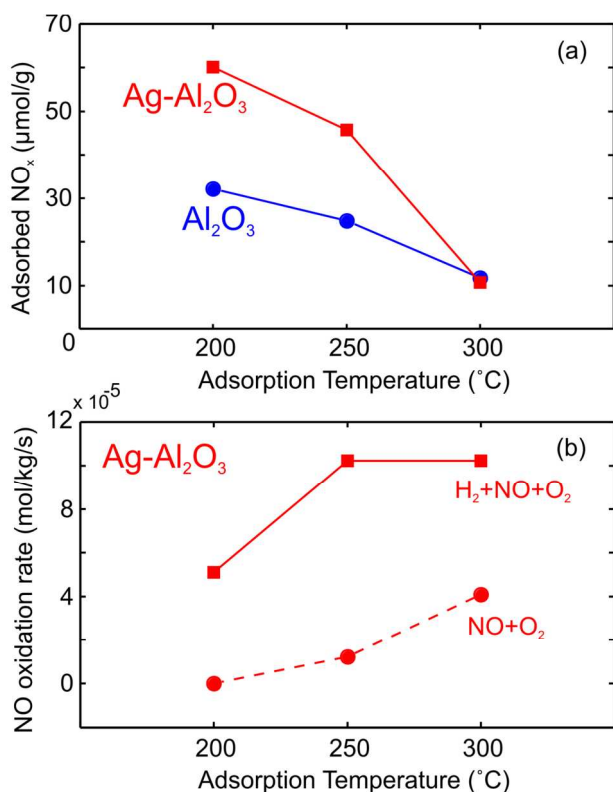
The HT desorption peak has often been proposed to result from the decomposition of monodentate nitrates that gave desorption of NO, NO<sub>2</sub> and O<sub>2</sub><sup>6, 23, 25</sup>. Here, only a small HT desorption peak was observed that gave mainly NO without O<sub>2</sub> desorption after NO-O<sub>2</sub> exposure. In this case the amount of monodentate nitrate species was likely too small in our monolithic sample to yield detectable O<sub>2</sub> desorption or they also partially left borrowed O atoms on the catalyst surface.

From TPD results for gas mixture of NO-O<sub>2</sub>-H<sub>2</sub> over Ag-Al<sub>2</sub>O<sub>3</sub> (Fig. 2b), it can be noted that along with higher activity for NO oxidation in the presence of H<sub>2</sub>, the LT peak observed in NO-O<sub>2</sub> TPD (Fig. 1b) was significantly suppressed and shifted towards the HT peak (Fig. 2b). However, in the case of Al<sub>2</sub>O<sub>3</sub> relatively little suppression in the LT peak was observed (Fig. 2d) along with no promotion of NO oxidation.

Due to the fact that the LT peak decomposed thermally at higher adsorption temperatures and was suppressed significantly in the presence of H<sub>2</sub> which both gave higher NO oxidation conversion, it is therefore reasonable to consider the LT peak to result from the decomposition of surface NO<sub>x</sub> species on the active sites. This also tends to indicate that Ag is needed to activate H<sub>2</sub> to suppress formation of surface NO<sub>x</sub> species that produce the LT peak. In addition, the active sites in the case of the Ag-Al<sub>2</sub>O<sub>3</sub> catalyst may involve Ag in close vicinity with Al<sub>2</sub>O<sub>3</sub> as assumed by others<sup>14, 31</sup>. By associating TPD and DRIFT, we suggest that H<sub>2</sub> eliminated surface nitrate species on active sites (LT peak) which is predominantly bidentate nitrate (1248 cm<sup>-1</sup>). Our result coincides with that of Chansai et al.<sup>14</sup> who used short time exposure (less than 120 s) in DRIFTS-MS study and suggested that the peak at 1255 cm<sup>-1</sup> assigned as monodentate nitrate in their work was the surface nitrate species located on the active part of the catalyst.

Further, the difference between the integrated LT NO<sub>x</sub> (NO+NO<sub>2</sub>) peaks from Fig. 1b (over Ag-Al<sub>2</sub>O<sub>3</sub>) and 1d (over Al<sub>2</sub>O<sub>3</sub>) can give an indication of the coverage of surface NO<sub>x</sub> species on active Ag sites. Figure 8a displays these results from TPD after NO-O<sub>2</sub> exposure between 200 and 300<sup>o</sup>C over both catalysts. As shown here, the coverage of surface NO<sub>x</sub> species on Ag sites decreased with higher temperature. By comparing with the amount of Ag available in the catalyst, the estimated amount of LT NO<sub>x</sub> on active sites (difference between Ag-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>) is much lower than the total amount of Ag (148 μmol/g). At 200 and 250<sup>o</sup>C, this LT NO<sub>x</sub> corresponded to 18% and 14% respectively of the total Ag, indicating that the dispersion of active sites may be comparable to these values.

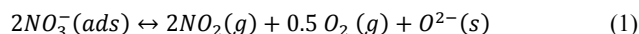
At 300<sup>o</sup>C, it could be observed that the amount of surface NO<sub>x</sub> species on Ag-Al<sub>2</sub>O<sub>3</sub> was more or less equal to Al<sub>2</sub>O<sub>3</sub>, thereby indicating that Ag sites were largely free from LT surface NO<sub>x</sub> species by 300<sup>o</sup>C. The differences in surface area for the Ag-Al<sub>2</sub>O<sub>3</sub> (188 m<sup>2</sup>/g) and Al<sub>2</sub>O<sub>3</sub> (233 m<sup>2</sup>/g) samples suggest that differences in their LT NO<sub>x</sub> adsorption cannot exactly quantify



**Fig. 8** The amount of surface NO<sub>x</sub> species from integration of LT desorption peak after NO<sub>2</sub>-O<sub>2</sub> adsorption over Ag-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> as shown earlier in Fig. 1 (upper panel, a) and reaction rate for NO oxidation and H<sub>2</sub>-assisted NO oxidation over Ag-Al<sub>2</sub>O<sub>3</sub> (lower panel, b)

the NO<sub>x</sub> on Ag sites. However even disregarding NO<sub>x</sub> adsorption on Al<sub>2</sub>O<sub>3</sub>, it is clear that at least 80% of Ag sites were freed from LT surface NO<sub>x</sub> species by 300°C compared to 200°C. Figure 8b compares the calculated reaction rates for NO oxidation (Fig. 1a) and H<sub>2</sub>-assisted NO oxidation (Fig. 2a). As seen here, the rate of NO<sub>2</sub> formation was always higher in the presence of H<sub>2</sub> at all temperatures, even at 300°C where Ag was largely free from the presumably inhibiting LT NO<sub>x</sub> species. If removal of inhibiting nitrate species was the only promoting role of H<sub>2</sub> for NO oxidation, one would expect the NO oxidation reaction rates with and without H<sub>2</sub> feed to be nearly equal at 300°C. If all inhibiting surface NO<sub>x</sub> species were thermally removed at 300°C, comparison of reaction rates at this temperature indicates that as much as 60% of total rate with H<sub>2</sub> feed could not be due to removal of inhibiting surface NO<sub>x</sub>. Therefore, this points out that H<sub>2</sub> should have additional promoting roles.

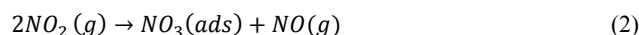
As shown in Fig. 2b, the shift of the NO<sub>x</sub> desorption peak upon introduction of H<sub>2</sub> over Ag-Al<sub>2</sub>O<sub>3</sub> was also accompanied by higher total quantities of NO<sub>x</sub> adsorbed and desorbed (Table 3) which was not observed for the case of Al<sub>2</sub>O<sub>3</sub>. H<sub>2</sub> induced NO<sub>x</sub> adsorption over Ag-Al<sub>2</sub>O<sub>3</sub> can then be related to the increase of the HT surface NO<sub>x</sub> species. Surface decomposition of the HT surface NO<sub>x</sub> species resulted in the release of NO<sub>2</sub> and O<sub>2</sub> and can be explained by equation (1) as has been addressed by Guo et al.<sup>7</sup>:



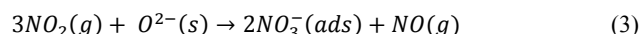
The mechanistic role of H<sub>2</sub> to promote NO<sub>x</sub> adsorption will be discussed further after following section.

### TPD studies following NO<sub>2</sub>-O<sub>2</sub> adsorption

The quantity and types of surface NO<sub>x</sub> species formed is also related to the NO<sub>x</sub> species composition of the gas phase and therefore TPD studies following NO<sub>2</sub>-O<sub>2</sub> adsorption were conducted. As seen from the DRIFT results in the lower panel of Fig. 6, formation of various surface nitrate species were detected upon exposure to NO<sub>2</sub> and O<sub>2</sub>. From Fig. 3a and 3c, formation of NO was observable during the NO<sub>2</sub>-O<sub>2</sub> adsorption over Ag-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>. By integration of the curves in Fig. 3a and 3c, the average ratio of total NO<sub>2</sub> uptake to total NO yield was 2.62 for Ag-Al<sub>2</sub>O<sub>3</sub> and 3 for Al<sub>2</sub>O<sub>3</sub>. Therefore, one can deduce that self-oxidation of NO<sub>2</sub> was likely to dominate during the adsorption step according to the following overall reaction:



However, surface oxides may also be involved by donating an O atom/ion similar to that discussed earlier in the first section of discussion part by the following overall reaction<sup>7</sup>:



As seen from reactions (2) and (3), the ratio of NO<sub>2</sub> adsorbed and NO released is 2 in reaction (2) and 3 in reaction (3). The ratios from the integration results fit well and suggest that both reactions are likely occurring during NO<sub>2</sub>-O<sub>2</sub> adsorption, with the reaction involving surface oxides as in reaction (3) being most dominant for Al<sub>2</sub>O<sub>3</sub>.

During the temperature ramp (Fig. 3b and 3d), it is interesting to note that TPD after NO<sub>2</sub>-O<sub>2</sub> adsorption over both Ag-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> gave broad peaks of NO<sub>2</sub> at temperatures exceeding 430°C, suggesting that NO<sub>2</sub> favors formation of HT surface NO<sub>x</sub> species. As seen from Fig. 3b and 3d, decomposition of the HT surface NO<sub>x</sub> species primarily produced NO<sub>2</sub> and O<sub>2</sub> as described in equation (1) over a range of temperatures from 350 to 545°C. The release of NO at more elevated temperatures above 500°C is probably related to a more extensive decomposition of the surface nitrates or even subsequent decomposition of the released NO<sub>2</sub> that is favored by thermodynamics. Both of these processes would also release gas phase O<sub>2</sub>.

### The role of H<sub>2</sub> to modify surface NO<sub>x</sub> species.

TPD results for NO-O<sub>2</sub>-H<sub>2</sub> (Fig. 2b) and NO<sub>2</sub>-O<sub>2</sub> (Fig. 3b) were similar, giving a substantial release of NO<sub>2</sub> and O<sub>2</sub> at a similar temperature range of the HT peaks. During adsorption of NO-O<sub>2</sub>-H<sub>2</sub> (Fig. 2a), production of NO<sub>2</sub> was always observable and from comparison with Fig. 1b and the low production of NO<sub>2</sub> during NO-O<sub>2</sub> adsorption, it is apparent that NO<sub>2</sub> production is linked to formation of the HT surface NO<sub>x</sub> species. Furthermore, additional experiments for NO<sub>2</sub>-O<sub>2</sub> TPD on Al<sub>2</sub>O<sub>3</sub> (Fig. 3d) gave a similar TPD profile for the same adsorption conditions with Ag-Al<sub>2</sub>O<sub>3</sub> (Fig. 3b), suggesting that most of the HT surface NO<sub>x</sub> species formed are located on the Al<sub>2</sub>O<sub>3</sub> support. Therefore, it was evident that the HT surface NO<sub>x</sub> species result from NO<sub>2</sub> adsorption and primarily located on the Al<sub>2</sub>O<sub>3</sub> support. It is also then likely that the HT surface NO<sub>x</sub> species formed on the Al<sub>2</sub>O<sub>3</sub> support are spectator surface species. As has been addressed earlier, these HT surface NO<sub>x</sub> species appear to be predominantly in the form of monodentate nitrates by associating the DRIFT and

TPD results. These findings agree well with those of Tamm et al.<sup>24</sup> who suggested one role of H<sub>2</sub> was to facilitate formation of monodentate nitrate that is not poisonous and likely to be located on Al<sub>2</sub>O<sub>3</sub>.

A mechanism of NO<sub>x</sub> storage by a spillover mechanism has been proposed<sup>8, 11, 24</sup>. An alternative mechanism of NO<sub>x</sub> storage by NO<sub>2</sub> readsorption on the Al<sub>2</sub>O<sub>3</sub> support has also been proposed by Johnson II et al.<sup>31</sup>. Based on the results of these TPD studies, it is indicative that the NO<sub>2</sub> readsorption mechanism is most probable for NO<sub>x</sub> storage on Al<sub>2</sub>O<sub>3</sub>, since formation of the HT surface NO<sub>x</sub> species was related to the presence of gas phase NO<sub>2</sub>. However, this does not negate the possibility that a spillover mechanism also contributes to NO<sub>x</sub> storage on Ag-Al<sub>2</sub>O<sub>3</sub>.

As described earlier for NO-O<sub>2</sub>-H<sub>2</sub> TPD over Al<sub>2</sub>O<sub>3</sub> (Fig. 2d), it is likely that the characteristics of the adsorbed surface NO<sub>x</sub> species are not the same over Ag-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>. Consequently, desorption of O<sub>2</sub> which was observed over Ag-Al<sub>2</sub>O<sub>3</sub> (Fig. 2b) was not observed over Al<sub>2</sub>O<sub>3</sub> (Fig. 2d) and NO<sub>x</sub> storage during adsorption of NO-O<sub>2</sub>-H<sub>2</sub> over Al<sub>2</sub>O<sub>3</sub> does not include formation of gas phase NO<sub>2</sub>.

### Mechanistic insights regarding C<sub>3</sub>H<sub>6</sub>-SCR and H<sub>2</sub>-assisted C<sub>3</sub>H<sub>6</sub>-SCR

TPD studies with C<sub>3</sub>H<sub>6</sub>-SCR and H<sub>2</sub>-assisted C<sub>3</sub>H<sub>6</sub>-SCR adsorption conditions were conducted over Ag-Al<sub>2</sub>O<sub>3</sub> to study how surface NO<sub>x</sub> species affect the NO<sub>x</sub> reduction performance. Reaction of surface NO<sub>x</sub> species with partially oxidized C<sub>3</sub>H<sub>6</sub> is considered as an important step to obtain high activity for C<sub>3</sub>H<sub>6</sub>-SCR over a Ag-Al<sub>2</sub>O<sub>3</sub> catalyst<sup>7, 32, 33</sup>.

It is interesting to note that by comparing the NO<sub>x</sub> desorption profile in C<sub>3</sub>H<sub>6</sub>-SCR (Fig. 4b) and NO oxidation (Fig. 1b), both of them have a similar profile with LT and HT NO<sub>x</sub> desorption peaks. However, for C<sub>3</sub>H<sub>6</sub>-SCR (Fig. 5b) the NO<sub>2</sub> desorption is very low probably due to the presence of adsorbed HC species that reduce the surface NO<sub>x</sub> species to NO during their decomposition and desorption. This presence of both LT and HT surface NO<sub>x</sub> species in approximately the same temperature ranges indicates that NO oxidation and C<sub>3</sub>H<sub>6</sub>-SCR should share some mechanistic features.

During the adsorption with C<sub>3</sub>H<sub>6</sub>-SCR conditions (Fig. 4a), NO<sub>x</sub> conversion at 300°C were clearly higher than 200 and 250°C. In addition, CO<sub>x</sub> desorption was observed during the temperature ramp (Fig. 4d) due to decomposition and oxidation of adsorbed and oxidized HC species. There tended to be more of these species at 300°C along with greater NO<sub>x</sub> reduction activity, suggesting that they are important intermediate species. Removal of the LT inhibiting surface NO<sub>x</sub> species at higher temperature (Fig. 4b) likely contributed to more formation of these intermediate species for the NO<sub>x</sub> reduction process<sup>7</sup>.

During the adsorption step for H<sub>2</sub>-assisted C<sub>3</sub>H<sub>6</sub>-SCR (Fig. 5a), higher NO<sub>x</sub> reduction activity was observed, reaching up to ~23% at 300°C. The improvement in NO<sub>x</sub> reduction activity was also accompanied by a significant decrease in the LT NO<sub>x</sub> desorption peak as can be seen by comparing Fig. 5b and 4b. At the same time, the HT NO<sub>x</sub> desorption peak increased remarkably. Therefore, again removal of the inhibiting LT surface NO<sub>x</sub> species, in this case aided by reaction with H<sub>2</sub>, coincided with the improved NO<sub>x</sub> reduction activity. Unlike in the case of NO-O<sub>2</sub>-H<sub>2</sub> (Fig. 2b) and NO<sub>2</sub>-O<sub>2</sub> (Fig. 3b) TPD, the increase of the HT peak

for H<sub>2</sub>-assisted C<sub>3</sub>H<sub>6</sub>-SCR (Fig. 5b) gave mostly NO desorption. Additionally, the O<sub>2</sub> desorption, however, was observed during desorption in all cases of TPD for NO-O<sub>2</sub>-H<sub>2</sub>, NO<sub>2</sub>-O<sub>2</sub> and H<sub>2</sub>-assisted C<sub>3</sub>H<sub>6</sub>-SCR. The larger production of NO for H<sub>2</sub>-assisted C<sub>3</sub>H<sub>6</sub>-SCR, probably resulted from the adsorbed HC which was oxidized by the adsorbed NO<sub>x</sub> species during their decomposition and desorption. From Figure 5b, it can also be seen that the HT NO<sub>x</sub> desorption peak had a broad shoulder towards lower temperatures. This shoulder probably results from the presence of adsorbed HC species acting as reductants and destabilizing the nitrate species to cause some lower temperature NO<sub>x</sub> decomposition.

As seen from Fig. 4d and 5d, the higher concentration of desorbed CO and CO<sub>2</sub> infers that H<sub>2</sub> had a promotional effect on low temperature C<sub>3</sub>H<sub>6</sub> activation. Hydrocarbon (HC) activation to form oxidized HC species itself is often suggested as a key step in HC-SCR over Ag-Al<sub>2</sub>O<sub>3</sub><sup>10, 13, 16</sup>. Greater formation of surface HC and oxidized HC in the presence of H<sub>2</sub> can be linked to the removal of inhibiting surface NO<sub>x</sub> species as suggested by the suppression of the LT surface NO<sub>x</sub> species also with H<sub>2</sub>. There was also a broadening of the CO<sub>x</sub> desorption peaks and a shift to lower desorption temperature with the addition of H<sub>2</sub> (comparing Fig. 5d and 4d) which suggests that a greater variety and possibly more reactive adsorbed hydrocarbon species with lower thermal stabilities were formed. This finding again points to the fact that H<sub>2</sub> may have other effects to promote the NO<sub>x</sub> reduction activity similar to the case for NO oxidation. The reaction rates for NO<sub>x</sub> conversion were 6.1 x 10<sup>-5</sup> and 22.5 x 10<sup>-5</sup> mol.kg<sup>-1</sup>.s<sup>-1</sup> at 300°C for C<sub>3</sub>H<sub>6</sub>-SCR and H<sub>2</sub>-assisted C<sub>3</sub>H<sub>6</sub>-SCR, respectively. It seems apparent from figure 4b that a large part of the inhibiting LT NO<sub>x</sub> species was removed by 300°C. Thus, again like that for NO oxidation as much as 73% of the C<sub>3</sub>H<sub>6</sub>-SCR activity from co-feeding H<sub>2</sub> could not be related to removal of inhibiting LT surface NO<sub>x</sub> species.

The amount of CO<sub>x</sub> desorbed did not monotonically decrease with higher temperature (Fig. 5d and 6d) as was always the case for adsorbed NO<sub>x</sub> species. Greater accumulation of adsorbed species producing CO<sub>x</sub> at higher temperature indicates that the reactions activating the HC to form oxygenated HC on the surface have relatively high activation energies. In other words, the activation energy to partially oxidize HC to form oxygenated HC surface species is higher than the activation energies of subsequent reactions between surface NO<sub>x</sub> species with the oxygenated HC species that leads to formation of N<sub>2</sub>. Greater accumulation of oxygenated HC surface species may also be due to less inhibiting nitrates covering the active sites where oxygenated HC are formed.

As seen from DRIFT results in figure 7, nitrate peaks assignable to monodentate, bidentate and bridging nitrates were detected for both C<sub>3</sub>H<sub>6</sub>-SCR and H<sub>2</sub>-assisted C<sub>3</sub>H<sub>6</sub> similar to the case with NO<sub>x</sub> adsorption (Fig. 6). By increasing temperature, the stability of monodentate nitrate (1546 cm<sup>-1</sup>) was clearly observed. Comparing the decreasing intensity of bidentate nitrate peaks for C<sub>3</sub>H<sub>6</sub>-SCR and H<sub>2</sub>-assisted C<sub>3</sub>H<sub>6</sub>-SCR, it was found that the rate of decrease with temperature is somewhat slower for the lower panel of Fig 7 (H<sub>2</sub>-assisted C<sub>3</sub>H<sub>6</sub>-SCR), indicating that the surface NO<sub>x</sub> species here were more stable which is in agreement with the TPD results. Further, it was also found that the relative

intensity of formate/acetate bands was higher for the H<sub>2</sub>-assisted case which agrees with the TPD observations (Fig.4d and 5d) that larger quantities of adsorbed HC species are present under the H<sub>2</sub>-assisted reaction conditions.

In this series of studies, it seems that the promoting role of H<sub>2</sub> appears to be only partially due to the removal of inhibiting surface NO<sub>x</sub> species. As a result the findings here support the possibility of other H<sub>2</sub> promoting roles as already described in the literature<sup>5, 10, 12, 13, 16, 22, 23</sup>. It has however been observed here that the formation of surface nitrate species in the absence of H<sub>2</sub> depends on the donation of oxygen from surface oxides. As a result the removal or prevented formation of these nitrate species caused by H<sub>2</sub> may be linked to some partial reduction of Ag species and thus formation of sites with enhanced activity. However an investigation of the merits of all other possible roles for H<sub>2</sub> to promote NO oxidation or NO<sub>x</sub> reduction is beyond the scope of this study and the methods used here.

## Conclusions

A series of TPD experiments have been conducted to investigate formation and stability of surface NO<sub>x</sub> species related to the promotional effect of H<sub>2</sub> for NO oxidation and C<sub>3</sub>H<sub>6</sub>-SCR. Formation of two general groups of surface NO<sub>x</sub> species were found to be present: a less thermally stable group of so called "LT surface NO<sub>x</sub> species" and a more thermally stable group of "HT surface NO<sub>x</sub> species". The following conclusions can be drawn from this study.

- The LT NO<sub>x</sub> desorption peak observed in this study could be attributed to the decomposition of surface NO<sub>x</sub> species formed on the active sites. It was apparent that Ag sites were largely free from these surface NO<sub>x</sub> species at and above 300°C. Elimination or decrease in quantities of these LT surface NO<sub>x</sub> species either thermally or by reaction with H<sub>2</sub> correlated with higher NO oxidation and NO<sub>x</sub> reduction conversion. However, as much as 60 % and 73 % of the activity for NO oxidation and NO<sub>x</sub> reduction respectively by co-feeding H<sub>2</sub> could not be related to removal of LT NO<sub>x</sub> surface species.
- The HT NO<sub>x</sub> desorption peak primarily corresponded to the decomposition of surface NO<sub>x</sub> species on the Al<sub>2</sub>O<sub>3</sub> support. Since the increase of surface NO<sub>x</sub> species formed on the Al<sub>2</sub>O<sub>3</sub> did not hinder NO oxidation and NO<sub>x</sub> reduction, the HT surface NO<sub>x</sub> species were mainly comprised of spectator surface species in the form of monodentate nitrates.
- H<sub>2</sub> facilitated formation of surface NO<sub>x</sub> species on the Al<sub>2</sub>O<sub>3</sub> support. It was indicative that the mechanism of NO<sub>x</sub> storage on the Al<sub>2</sub>O<sub>3</sub> support was via NO<sub>2</sub> readsorption, but spillover may also play a role.
- H<sub>2</sub> facilitated formation of oxygenated HC on the surface that may be aided by removal of inhibiting surface NO<sub>x</sub> species on active sites.
- Formation of the LT surface nitrate species depended on the donation of oxygen from surface oxides. As a result the removal or prevented formation of these nitrate species caused by H<sub>2</sub> may entail some partial reduction of Ag species and be linked to enhanced C<sub>3</sub>H<sub>6</sub>-SCR and NO oxidation activity.

From this study, it was seen that the quantities of surface NO<sub>x</sub>

species removed from the active sites were small compared to the amount simultaneously stored as spectator species mainly on the alumina support. Therefore, the dual role of H<sub>2</sub> to both eliminate inhibiting surface NO<sub>x</sub> species from active sites and promote NO<sub>x</sub> storage was elucidated.

## Acknowledgements

This work has been financially supported by the Swedish Research Council with grant number 621-2011-3926 and partly within the Competence Centre for Catalysis, which is hosted by Chalmers University of Technology and financially supported by the Swedish Energy Agency and the member companies AB Volvo, ECAPS AB, Haldor Topsøe A/S, Scania CV AB, Volvo Car Corporation AB and Wärtsilä Finland Oy. MMA acknowledged Fredrik Gunnarsson for collaboration in preparing Ag-Al<sub>2</sub>O<sub>3</sub> catalyst.

## Notes and references

- T. Miyadera, *Appl. Catal. B: Environ.*, 1993, **2-3**, 199-205.
- K.-i. Shimizu and A. Satsuma, *Phys. Chem. Chem. Phys.*, 2006, **8**, 2677-2695.
- E. Seker, J. Cavataio, E. Gulari, P. Lorpongpaiboon and S. Osuwan, *Appl. Catal. A: Gen.*, 1999, **183**, 121-134.
- M. Yamaguchi, I. Goto, Z. M. Wang and M. Kumagai, *Stud. Surf. Sci. Catal.*, 1999, **121**, 371-374.
- S. Satokawa, J. Shibata, K.-i. Shimizu, A. Satsuma and T. Hattori, *Appl. Catal. B: Environ.*, 2003, **42**, 179-186.
- S. Kameoka, Y. Ukisu and T. Miyadera, *Phys. Chem. Chem. Phys.*, 2000, **2**, 367-372.
- Y. Guo, M. Sakurai and H. Kameyama, *Appl. Catal. B: Environ.*, 2008, **79**, 382-393.
- N. Sadokhina, D. Doronkin, P. Pributkov, V. Bukhtiyarov, R. Kvon and A. Stakheev, *Top. Catal.*, 2011, **54**, 1190-1196.
- X. She and M. Flytzani-Stephanopoulos, *J. Catal.*, 2006, **237**, 79-93.
- J. Shibata, K.-i. Shimizu, S. Satokawa, A. Satsuma and T. Hattori, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2154-2160.
- R. Brosius, K. Arve, M. H. Groothaert and J. A. Martens, *J. Catal.*, 2005, **231**, 344-353.
- J. P. Breen, R. Burch, C. Hardacre, C. J. Hill and C. Rioche, *J. Catal.*, 2007, **246**, 1-9.
- Y. Guo, J. Chen and H. Kameyama, *Appl. Catal. A: Gen.*, 2011, **397**, 163-170.
- S. Chansai, R. Burch and C. Hardacre, *J. Catal.*, 2012, **295**, 223-231.
- N.A. Sadokhina, D.E. Doronkin, G.N. Baeva, S. Dahl, A.Y. Stakheev, *Top. Catal.*, 2013, **56**, 737-744.
- J. P. Breen and R. Burch, *Top. Catal.*, 2006, **39**, 53-58.
- P. Sazama, L. Capek, H. Drobna, Z. Sobalik, J. Dedecek, K. Arve and B. Wichterlova, *J. Catal.*, 2005, **232**, 302-317.
- S. T. Korhonen, A. M. Beale, M. A. Newton and B. M. Weckhuysen, *J. Phys. Chem. C*, 2011, **115**, 885-896.
- U. Bentrup, M. Richter and R. Fricke, *Appl. Catal. B: Environ.*, 2005, **55**, 213-220.
- R. Burch, J. P. Breen, C. J. Hill, B. Krutzsch, B. Konrad, E. Jobson, L. Cider, K. Eränen, F. Klingstedt and L. E. Lindfors, *Top. Catal.*, 2004, **30-31**, 19-25.
- M. M. Azis, H. Härelind and D. Creaser, *Chem. Eng. J.*, 2013, **221**, 382-397.
- K.-i. Shimizu, K. Sawabe and A. Satsuma, *Cat. Sci. Technol.*, 2011, **1**, 331-341.
- P. S. Kim, M. K. Kim, B. K. Cho, I. S. Nam and S. H. Oh, *J. Catal.*, 2013, **301**, 65-76.
- S. Tamm, N. Vallim, M. Skoglundh and L. Olsson, *J. Catal.*, 2013, **307**, 153-161.
- X. Zhang, H. He, H. Gao and Y. Yu, *Spectrochim. Acta Part A*, 2008, **71**, 1446-1451.

26. F.C. Meunier, J.P. Breen, V. Zuzaniuk, M. Olsson, J.R.H. Ross, *J. Catal.*, 1999, **187**, 493-505.
27. H. Kannisto, H. H. Ingelsten and M. Skoglundh, *J. Mol. Catal. A-Chem.*, 2009, **302**, 86-96.
- 5 28. H. Härelind, F. Gunnarsson, S. M. S. Vaghefi, M. Skoglundh and P. A. Carlsson, *ACS Catal.*, 2012, **2**, 1615-1623. 65
29. X. L. Zhang, Y. B. Yu and H. He, *Appl. Catal. B: Environ.*, 2007, **76**, 241-247.
30. S. Klacar, A. Hellman, I. Panas and H. Grönbeck, *J. Phys. Chem. C*, 2010, **114**, 12610-12617. 10
31. W. L. Johnson II, G. B. Fisher and T. J. Toops, *Catalysis Today*, 2012, **184**, 166-177. 70
32. T. Furusawa, L. Lefferts, K. Seshan and K. Aika, *Appl. Catal. B: Environ.*, 2003, **42**, 25-34.
- 15 33. Y. Yu, X. Zhang and H. He, *Appl. Catal. B: Environ.*, 2007, **75**, 298-302.

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