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Adsorption chemistry of NO_x on Ag/Al_2O_3 catalyst for selective catalytic reduction of NO_x using hydrocarbons

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Abstract

Ag/Al_2O_3 is an active catalyst for selective catalytic reduction (SCR) of NO_x using long paraffins as reducing agents. In view of the important role of surface nitrates in this catalytic chemistry, their formation on the Ag/Al_2O_3 catalyst, i.e. on the alumina support and on the silver species, was quantified in this study under typical reaction conditions of 500–1000 ppm NO_x, 6% O_2 and 12% H_2O. The NO_x adsorption capacity and the stoichiometry of nitrate formation and elimination reactions were determined as function of the temperature and the composition of the NO_x using volumetric determinations in a flow system. The silver chemistry was investigated using in situ DR UV–vis spectroscopy. In the presence of water, nitrate formation out of NO_2 proceeds according to two different mechanisms depending on the state of silver as Ag(0) or Ag(I) on the catalyst. Minute concentrations of hydrogen (3500 ppm) are responsible for Ag(I) reduction. The study reveals the origin of the promotion of the low temperature SCR-NO_x activity of Ag/Al_2O_3 by hydrogen. Hydroxylation–dehydroxylation of the alumina surface of Ag/Al_2O_3 catalyst was found to be an oscillating reaction, whereas the alumina support itself did not display this phenomenon.

Keywords: Ag/Al_2O_3; Hydrogen effect; Surface nitrates; Oscillating reaction; Silver clusters

1. Introduction

Alumina supported silver (Ag/Al_2O_3) exhibits high catalytic activity in selective catalytic reduction of NO_x with hydrocarbons in oxygen containing gas mixtures (*HC-SCR of* NO_x). *HC-SCR of* NO_x with Ag/Al_2O_3 catalyst has been demonstrated using propene [1–4], long paraffins [5–7] and alcohols [6,8–11] as reducing agents. The light-off temperature of the Ag/Al_2O_3 catalyst is strongly dependent on the nature of the reducing agent [12]. The highest catalytic activities were reached when using long-chain paraffins typical of diesel fuel as reductants, which makes Ag/Al_2O_3 a candidate for application in purification of heavy-duty diesel engine exhaust [12]. The nature of the active silver species, the reaction mechanism and the origin of promotion by hydrogen of *HC-SCR of* NO_x at low temperatures are subjects of an ongoing discussion in literature [5,6,8,11–18].

The speciation of silver in Ag/Al_2O_3 catalysts has been thoroughly investigated using a variety of techniques including H_2-TPR, X-ray absorption spectroscopies, XRD, UV–vis spectroscopy and TEM. On calcined Ag/Al_2O_3 catalyst with Ag content optimized with respect to activity in *HC-SCR of* NO_x, silver is predominantly in the Ag(I) state [5,12,13,15,19–21]. The optimum Ag content is typically around 2 wt% depending on alumina type and specific surface area. The chemical environment of Ag(I) has been interpreted as an oxide phase [19,21] or as a silver aluminate phase [14,15]. Iglesias-Juez et al. observed that active Ag/Al_2O_3 catalysts contain small silver aluminate particles with tetrahedral symmetry like in β-$AgAlO_2$ phases [14]. Satsuma et al. applied in situ UV–vis DRS to investigate the dispersion of silver in oxidizing and reducing atmospheres on

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Ag/Al_2O_3 at 250 °C [22]. In inert gas spiked with 5000 ppm H_2 and 10% O_2, Ag(I) ions were reduced and aggregated into silver clusters, which could be re-oxidized and dispersed in the presence of NO and O_2. The relative reaction rate of reduction as compared to oxidation increased with increasing silver content. Even trace amounts of reducing agents such as 500 ppm propene in the presence of 2.5% O_2 caused reduction of part of the silver [15]. Above the optimum silver content of Ag/Al_2O_3, large metallic silver particles are formed [5,15,22]. Besides crystalline silver phases, large clusters of amorphous or poorly crystallized silver phases have been detected after exposure of the catalyst to a gas mixture for performing *HC-SCR of* NO_x by means of TEM [1,15,19]. At Ag contents of 5 wt% and higher, large silver metal particles form irreversibly upon reduction of the catalyst. These large silver particles are less active in *HC-SCR of* NO_x [22].

Bogdanchikova et al. revealed that oxidation of NO with O_2 into NO_2 is catalyzed by crystalline metallic silver, whereas *HC-SCR of* NO_x is promoted by Ag(I) [15]. Ag/Al_2O_3 effective for *HC-SCR of* NO_x is inactive in NO to NO_2 oxidation with O_2 [15] suggesting that on Ag/Al_2O_3 the oxidation of NO into NO_2 is not a crucial reaction step in *HC-SCR of* NO_x as it is on other catalysts [23]. Several authors adhere to a reaction mechanism in which hydrocarbon reducing agent is activated through partial oxidation. This activated hydrocarbon is proposed to react with nitrates on the catalyst surface into reaction intermediates that finally lead to nitrogen and carbon oxides [5,14,24–27]. Some reaction steps of the *HC-SCR of* NO_x reaction occur in homogeneous gas phase [6]. Oxygenated hydrocarbons adsorbed on the catalyst surface were observed using in situ FTIR spectroscopy, viz. acetate in *HC-SCR of* NO_x using propene [13,16,28], hexane [5], octane [6,17] and decane on $Ag/Rh/Al_2O_3$ [26]; an enolic species in the presence of propene, ethanol and acetaldehyde on $Ag/Pd/Al_2O_3$ [25,26]; formate in the presence of octane [17] as well as carbonates in many instances. Reaction between oxygenated hydrocarbon and NO_x leads to formation of isocyanate (–NCO) species observed with in situ DRIFT spectroscopy and assumed to be key reaction intermediates [8]. In that study acetate species accumulated on the catalyst during reaction and were not considered to be reaction intermediates [8]. Yu et al. confirmed that enolic species are more reactive toward NO_x than acetate species [11]. The absence of appreciable activity of Ag/Al_2O_3 at temperatures below 250 °C was ascribed to inhibition of active sites by adsorbed nitrates [5,13,24,29].

Satokawa et al. discovered that the low temperature activity of Ag/Al_2O_3 in *HC-SCR of* NO_x was boosted by addition of minute quantities of hydrogen gas [13,20]. In *HC-SCR of* NO_x using octane at 250 °C, hydrogen was found to promote formation and accumulation of organic cyanide species that easily reduce NO_x. Hydrogen prevented accumulation of AgCN species that act as a poison [17]. Furthermore, in the presence of hydrogen the accumulation of acetate on the catalyst was much less pronounced [17]. On the other hand, in studies on *HC-SCR of* NO_x using propane, Shibata et al. and Satokawa et al. observed the opposite effect, viz. a remarkable increase of adsorbed acetate formation at 300 °C in the presence of hydrogen [13,16]. The presence of hydrogen in the reaction feed resulted in an increased formation rate of nitrates on the catalyst surface [16,21]. A comparison of the formation and consumption rates of acetates and nitrates led to the conclusion that the promotion effect of hydrogen in *SCR of* NO_x using propane was due to the promotion of partial oxidation of propane into acetate [16].

This literature overview reveals that many authors emphasize the role of adsorbed nitrates on Ag/Al_2O_3 and related catalysts [5,11,14,16,18,21,24,28]. In view of their presumed important role, in this work we investigated in detail the surface nitrate formation on Ag/Al_2O_3 catalyst in the presence and absence of hydrogen. Most of the Ag/Al_2O_3 catalyst characterization work reported in literature was done using dry gases, whereas *HC-SCR of* NO_x is practiced in the presence of water. The NO_x adsorption chemistry of Ag/Al_2O_3 catalyst can be expected to be dependent on the presence of water. In this work we investigated the adsorption chemistry of NO and NO_2 on Ag/Al_2O_3 catalyst in the presence of water vapor. Because of the presence of water in the gas streams, the experimental approaches had to be limited to volumetric methods and in situ UV–vis spectroscopy. The weight of pretreated catalyst was monitored under oxygen and water containing helium stream in an ultra-precision magnetic suspension balance (Rubotherm).

2. Experimental

Ag/Al_2O_3 with 2 wt% Ag loading was prepared at Åbo Akademi University by impregnation of a commercial Al_2O_3 support (LaRoche Industries Inc.). The support material was ground to a particle size of < 250 µm and mixed with a 0.022 M $AgNO_3$ solution followed by drying and calcination at 550 °C for 3 h [6]. In the *SCR of* NO_x experiment, the catalyst bed volume was 0.6 ml (400 mg). Catalyst pellets of 0.25–0.5 mm were loaded in a quartz tube with inner diameter of 9 mm and held in position between two quartz wool plugs. In the volumetric adsorption experiments typically 1.5 ml (1000 mg) of catalyst pellets were used. The reactor tube was mounted in a vertical tubular furnace and connected to a flow system. Helium was used as inert gas in all gas mixtures used for catalyst pretreatment and adsorption studies. The total gas flow rate was 300 ml per minute. The B.E.T. specific surface area of the original alumina and of Ag/Al_2O_3 catalyst, measured by means of nitrogen adsorption following evacuation at 400 °C overnight, was 358 and 187 $m^2\,g^{-1}$, respectively. Reduced Ag/Al_2O_3 catalyst was obtained by reduction at 300 °C in hydrogen gas containing 12% H_2O. In the NO_x adsorption and desorption experiments, the catalyst heating rate was 10 $°C\,min^{-1}$. Catalyst cooling was passive so that the temperature decrease was ca. −5 °C $\min^{-1}$ gradually slowing to lower rates when approaching the lowest investigated temperature, viz. 150 °C. NO and NO_2 concentrations in the gas stream were measured with an internally heated chemiluminescence detector (Ecophysics 700 EL ht). The formation and decomposition of nitrates was monitored by optical fiber in situ UV–vis spectroscopy in the diffuse reflectance (DR) mode. The spectroscopic setup consisted of a quartz reactor tube holding catalyst inside a tubular furnace, a UV–vis light source (Top Sensor Systems DH-2000 deuterium-halogen light source) and a photodiode array detector (Ocean Optics SD 2000) connected to the catalyst via optical fibers. The optical fiber probe was mounted outside the reactor tube and pointed at the middle of the catalyst bed. Before each new experiment, the UV–vis spectrum of a reactor containing alumina pellets – the white reference – was recorded and subsequently subtracted of all measured Ag/Al_2O_3 spectra. The UV–vis spectra were recorded through the quartz reactor wall [30]. Typically, one spectrum in the 250–500 nm region is the result of the superposition of 1000 scans, each taking 53 ms. The total gas flow rate was 50 ml $\min^{-1}$ and the catalyst volume 0.375 ml (250 mg). Gravimetric experiments were conducted in an ultra-precision magnetic suspension balance (Rubotherm).

3. Results and discussion

3.1. *HC-SCR of NO_x experiment*

The investigated Ag/Al_2O_3 sample is an active *HC-SCR of NO_x* catalyst [6]. The performance in *HC-SCR of NO_x* using decane is illustrated in Fig. 1. NO_x conversion into N_2 in a gas mixture made up of helium with 1000 ppm NO, 600 ppm $C_{10}H_{22}$, 6% O_2, 350 ppm CO, 10% CO_2 and 12% H_2O was determined in the temperature range 150–550 °C at 50 °C intervals. Below 200 °C, little NO_x conversion occurred. NO_x conversion close to 100% was reached between 300 and 400 °C. The NO_x conversion decreased again above 400 °C and reached ca. 60% at 550 °C. At these high temperatures, the hydrocarbon is partially lost in catalytic combustion reactions competing with *HC-SCR of NO_x*.

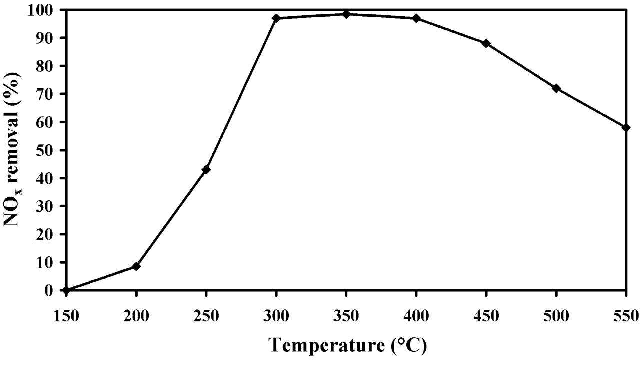

Fig. 1. NO_x conversion into N_2 on Ag/Al_2O_3 catalyst at 50 °C intervals in *SCR of NO_x*. Gas composition: 1000 ppm NO, 600 ppm $C_{10}H_{22}$, 6% O_2, 12% H_2O, 10% CO_2 and 350 ppm CO at GHSV: 30,000 h^{-1}.

3.2. *Volumetric NO_x adsorption experiments in absence of hydrogen*

The adsorption of NO_x was studied in the reactor unit using gas mixtures without reducing agent. Ag/Al_2O_3 pretreated at 400 °C in oxidizing gas comprising 6% O_2 and 12% H_2O was cooled to 150 °C in a flow of the same gas. The gas composition was subsequently altered to 1000 ppm NO, 6% O_2 and 12% H_2O and the NO_x adsorption monitored. The NO_x concentration in the reactor outlet dropped very briefly below the inlet value of 1000 ppm. The quantity of retained NO_x corresponded to the filling of the empty volume of the reactor. It was concluded that at 150 °C Ag/Al_2O_3 did not adsorb any NO in the presence of 12% water in the gas mixture. There was no transformation of NO into NO_2. Similar experiments performed at temperatures up to 400 °C confirmed the inertness of Ag/Al_2O_3 against NO in the presence of 12% water. Notice that in similar experiments monitored by IR spectroscopy in absence of water reported in literature [5,16], NO and O_2 did react with the Ag/Al_2O_3 surface and gave rise to nitrate formation.

In a subsequent experiment, catalyst was pretreated at 400 °C in oxidizing gas (6% O_2 and 12% H_2O), cooled to 150 °C and exposed to a gas stream containing 500 ppm NO_2, 500 ppm NO, 6% O_2 and 12% H_2O. The evolution of the NO, NO_2 and NO_x concentration in the gas stream at the reactor outlet after the switching of the gas composition from pretreatment to NO_x containing gas is shown in Fig. 2. First, there was for a short time strong NO_x uptake revealed by the outlet NO_x concentration starting at the zero level. NO_2 remained absent in the adsorber outlet for some 40 min while the NO outlet concentration leveled around 669 ± 7 ppm, i.e. significantly above the inlet value of 500 ppm. Saturation of the Ag/Al_2O_3 sample with NO_x detected by the outlet NO and NO_2 concentrations regaining the inlet values was reached after ca. 90 min.

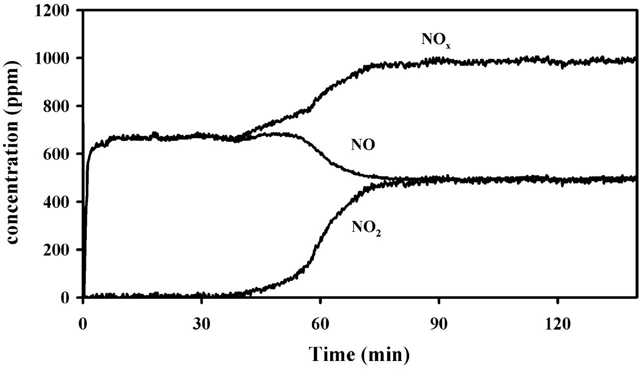

Fig. 2. Time course of the NO, NO_2 and NO_x concentrations at outlet of bed of Ag/Al_2O_3 catalyst contacted at 150 °C with a gas mixture composed of 500 ppm NO_2, 500 ppm NO, 6% O_2 and 12% H_2O in helium.

Table 1
Volumetric determination of NO_x adsorption and desorption on Ag/Al_2O_3 catalyst and Al_2O_3 support

NO_x in gas mixture[a]	Catalyst												
	Ag/Al_2O_3 500 ppm NO_2 (A)							Ag/Al_2O_3 500 ppm NO_2, 500 ppm NO (B)		Al_2O_3 500 ppm NO_2 (A)	Ag/Al_2O_3 500 ppm NO_2, 3500 ppm H_2 (C)		
Temperature (°C)	100	150	200	250	300	350	400	100	150	150	100	150	200
1 $NO_{x\,ads}$[b] ($\mu mol\,g^{-1}$)	549	383	265	170	111	56	39	446	305	614	202	211	552
2 $NO_{2\,react}/NO_{release}$[c]	3.0	3.0	3.1	3.0	3.1	ND[d]	ND	3.2	3.1	3.0	ND	ND	ND
3 $NO_{x\,des}$[b] (Step 1) ($\mu mol\,g^{-1}$)	205	187	170	ND	ND	ND	ND	172	194	383	148	94	207
4 $NO_{2\,release}/NO_{react}$[c]	2.4	2.4	2.5	ND	ND	ND	ND	2.2	2.6	3.1	ND	ND	ND
5 $NO_{x\,des}$[b] (Step 2) ($\mu mol\,g^{-1}$)	339	194	94	ND	ND	ND	ND	274	171	233	59	126	313
6 $NO_{2\,release}/NO_{react}$[c]	3.0	2.9	2.7[e]	ND	ND	ND	ND	2.8	2.7	3.0	ND	ND	ND
7 $NO_{x\,des}$[b] (total) ($\mu mol\,g^{-1}$)	544	381	264	170	109	63	32	446	311	616	207	220	520

[a] Composed of 6% O_2 and 12% H_2O in helium.
[b] Error on values estimated at 2%.
[c] Error on values estimated at 4%.
[d] ND: not determined.
[e] Influenced by oxidation of NO into NO_2.

The NO_x adsorption ($NO_{x\,ads}$) capacity in the experiment of Fig. 2 was ca. 305 $\mu mol\,g^{-1}$. From the NO_2 and NO of the feed, it is the NO_2 that is selectively adsorbed. In the period from 2 to 90 min, there was transformation of NO_2 into NO. In the period of constant NO outlet concentration from 2 to 40 min, the NO concentration was raised by 169 ± 7 ppm. Considering that in this period the 500 ppm of NO_2 in the feed reacted entirely, the molar ratio of reacted NO_2 to NO formation was ca. 3.0. Over the entire 90 min period in which NO_x adsorption occurred, the molar ratio of reacted NO_2 over desorbed NO ($NO_{2\,react}/NO_{release}$) was also around 3.0.

NO_x adsorption capacities and $NO_{2\,react}/NO_{release}$ values in gas streams containing 500 ppm NO_2, 6% O_2 and 12% H_2O were determined at 50 °C intervals in the temperature range 100–400 °C (Table 1, column 2, rows 1 and 2). The NO_x adsorption capacity was ca. 549 $\mu mol\,g^{-1}$ at 100 °C, decreasing to ca. 39 $\mu mol\,g^{-1}$ at 400 °C. In the temperature range 100–300 °C, the molar ratio of $NO_{2\,react}/NO_{release}$ was close to the integer value of 3. At 350 and 400 °C, the occurrence of some catalytic decomposition of NO_2 into NO and O_2 impeded correct determination of the stoichiometry of NO_2 adsorption and NO release.

The release of one molecule of NO per three molecules of reacted NO_2 reflects the reaction stoichiometry of NO_2 disproportionation into nitric acid and NO:

$$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO. \tag{1}$$

Note that in the absence of water, the NO_2 adsorption chemistry on Ag/Al_2O_3 is entirely different. Surface hydroxyl groups (HO-surf) were proposed to be involved in nitric acid formation according to [14]:

$$NO_2 + \text{HO-surf} \rightleftharpoons HNO_3\text{-surf}. \tag{2}$$

On dehydroxylated alumina surfaces, nitrate and nitrite formation was proposed to involve framework oxygen atoms, O^{2-}, according to [31]:

$$3NO_2 + O^{2-} \rightleftharpoons 2(NO_3^-) + NO, \tag{3}$$

$$2NO_2 + O^{2-} \rightleftharpoons NO_3^- + NO_2^-. \tag{4}$$

Nitric acid formed on the hydrated surface of the catalyst according to Eq. (1) is expected to react with basic sites into surface nitrates. The nature of the nitrates could be determined and their concentration quantified using temperature programmed experiments as follows. Catalyst saturated with nitrate at 150 °C in a gas stream containing 500 ppm NO_2, 6% O_2 and 12% H_2O was flushed at the same temperature with a gas stream comprising 1000 ppm NO, 6% O_2 and 12% H_2O (Fig. 3). Immediate consumption of NO and release of NO_2 ensued. The concentration of desorbing NO_2 first reached a peak value of 1800 ppm, decreased subsequently with time and was terminated after

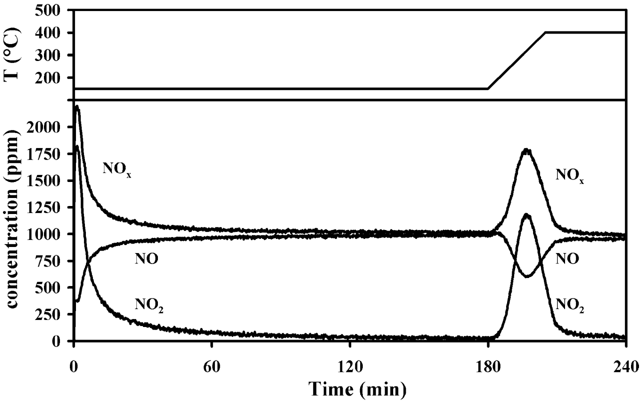

Fig. 3. Time course of the catalyst temperature and of the NO, NO_2, and NO_x concentrations in outlet of Ag/Al_2O_3 catalyst bed previously saturated with nitrates at 150 °C in a gas stream of 500 ppm NO_2, 6% O_2 and 12% H_2O and contacted with a gas mixture composed of 1000 ppm NO, 6% O_2 and 12% H_2O in helium.

some 180 min. The amount of NO_x that desorbed corresponded to ca. 187 $\mu mol\,g^{-1}$ (Table 1, line 3). This value matches within experimental error with the Ag content of 185 $\mu mol\,g^{-1}$. From this correspondence, it is concluded that upon exposure of oxidized catalyst to NO_2, oxygen and water, all Ag(I) is converted into nitrate that can be eliminated by exposing the catalyst to a wet gas stream with NO. Further evidence for silver nitrate formation was obtained from in situ DRS UV–vis experiments and will be presented later. The formation of silver nitrate according to the following two reactions can explain the net release of one mol of NO_x per mol of $AgNO_3$ reacted:

$$2AgNO_3 + NO \rightleftharpoons 3NO_2 + Ag_2O, \tag{5}$$

$$AgNO_3 + NO \rightleftharpoons 2NO_2 + Ag(0). \tag{6}$$

The molar ratio of $NO_{2\,release}/NO_{react}$ according to Eqs. (5) and (6) is 3 and 2, respectively. Thus the $NO_{2\,release}/NO_{react}$ ratio can be used to probe the formation of Ag(I), represented as Ag_2O in Eq. (5), versus Ag(0). The experimental ratio of $NO_{2\,release}/NO_{react}$ was 2.4 (Table 1, line 4), which is intermediate between 2 and 3, revealing that the $AgNO_3$ decomposition through reaction with NO gave rise to a mixture of Ag(I) and Ag(0).

In the experiment of Fig. 3 after elimination of silver nitrate at 150 °C, the temperature was raised to 400 °C under gas stream of 1000 ppm NO, 6% O_2 and 12% water. Additional NO_2 desorption and concomitant NO consumption occurred upon heating, suggesting decomposition of additional nitrates. Given that all silver nitrate had already been eliminated, these nitrates decomposing at temperatures above 150 °C must be located on the alumina support. The reaction of aluminum nitrate with NO corresponds to:

$$2Al(NO_3)_3 + 3NO \rightleftharpoons 9NO_2 + Al_2O_3. \tag{7}$$

In the presence of water, the Al_2O_3 surface obtained after elimination of the nitrates will react with water and will be hydroxylated. The experimental $NO_{2\,release}/NO_{react}$ ratio was 2.9 (Table 1, line 6), and close to the theoretical ratio of 3 according to Eq. (7).

The experiment of Fig. 3 corroborates the existence of two kinds of adsorbed nitrate, viz. silver nitrate and aluminum nitrate. Discrimination between both types is possible based on the decomposition temperature upon exposure to NO gas being 150 °C for silver nitrate and above 200 °C for aluminum nitrate. Silver and aluminum nitrate formation in gas streams containing 500 ppm NO_2, 6% O_2 and 12% H_2O at 100 and 200 °C was quantified through reaction with NO (Table 1, rows 3–6). At 100 and 200 °C in gas streams containing 500 ppm NO_2, 6% O_2 and 12% H_2O, the NO_x desorption in Step 1 was ca. 205 and 170 $\mu mol\,g^{-1}$, respectively. These quantities are close to the silver content of the catalyst (185 $\mu mol\,g^{-1}$) suggesting that this NO_x desorption essentially stems from silver nitrate. The molar ratio of $NO_{2\,release}/NO_{react}$ was 2.4–2.5, suggesting reaction of silver nitrate into Ag(0) and Ag(I) species according to a combination of Eqs. (5) and (6). The formation of aluminum nitrate, derived from Step 2 NO_x desorption, decreased with temperature from 339 $\mu mol\,g^{-1}$ at 100 °C to 94 $\mu mol\,g^{-1}$ at 200 °C (Table 1, line 5). Step 2 NO_x desorption starting at 100 °C involved reaction of 1 mol of NO per 3 mol of NO_2 released (Table 1, line 6). The stoichiometry of NO reaction to NO_2 desorption could not be determined accurately in the experiment at 200 °C, because of the presence of catalytic activity converting some NO into NO_2 at the high temperature part of the NO_x desorption peak. The total NO_x release in Step 1 (owing to elimination of silver nitrate) together with Step 2 (owing to aluminum nitrate) (Table 1, line 7) was in good agreement with the adsorbed amount (Table 1, line 1), showing that all nitrates were quantitatively eliminated through reaction with NO.

Subsequently, nitrate formation was investigated in the presence of a mixture of NO_2 and NO in the gas phase like in the experiment of Fig. 2. The catalyst surface was reacted with a gas mixture containing 500 ppm NO_2 and 500 ppm NO next to 6% O_2 and 12% H_2O (Table 1, column 3, line 1). In the presence of 500 ppm NO next to 500 ppm NO_2, the nitrate capacity of Ag/Al_2O_3 was lower than in the presence of 500 ppm NO_2 only, viz. 305 $\mu mol\,g^{-1}$ compared to 383 $\mu mol\,g^{-1}$ at 150 °C and 446 $\mu mol\,g^{-1}$ compared to 549 $\mu mol\,g^{-1}$ at 100 °C. With NO present next to NO_2, the formation of nitric acid and nitrates according to Eq. (1) is thermodynamically less favorable. This treatment leads to quantitative transformation of all silver into silver nitrate, and to formation of ca. 171 and 274 $\mu mol\,g^{-1}$ aluminum nitrate, respectively (Table 1, column 3, lines 3 and 5).

The elimination of nitrates from Ag/Al_2O_3 samples provided with nitrates at 150 °C using a gas stream of 6% O_2 and 12% H_2O together with NO_x fed either as 500 ppm NO_2 (A) or 500 ppm NO and 500 ppm NO_2 (B) was compared in Figs. 4a and 4b. Fig. 4 shows the evolution of NO, NO_2, and NO_x concentrations in the reactor outlet during nitrate elimination through reaction with a gas stream comprising 1000 ppm NO, 6% O_2 and 12% H_2O at 150 °C. The sample on which the nitrates were formed out of 500 ppm NO_2

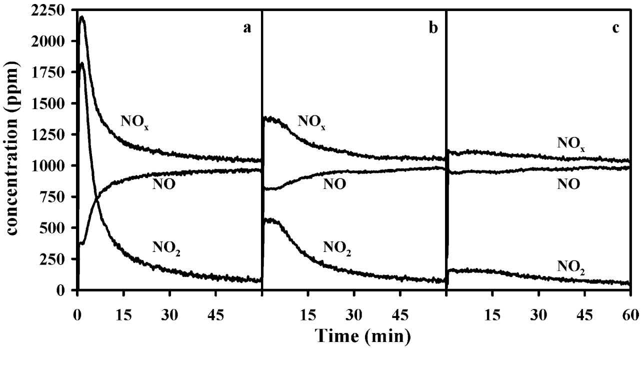

Fig. 4. Time course of the NO, NO_2, and NO_x concentrations in outlet of nitrate saturated Ag/Al_2O_3 catalyst bed contacted at 150 °C with a gas stream made up of helium with 1000 ppm NO, 6% O_2 and 12% H_2O. Nitrate formation conditions: (a) helium containing 500 ppm NO_2, 6% O_2 and 12% H_2O; (b) 500 ppm NO_2 + 500 ppm NO, 6% O_2 and 12% H_2O and (c) 500 ppm NO_2 + 3500 ppm H_2, 6% O_2 and 12% H_2O.

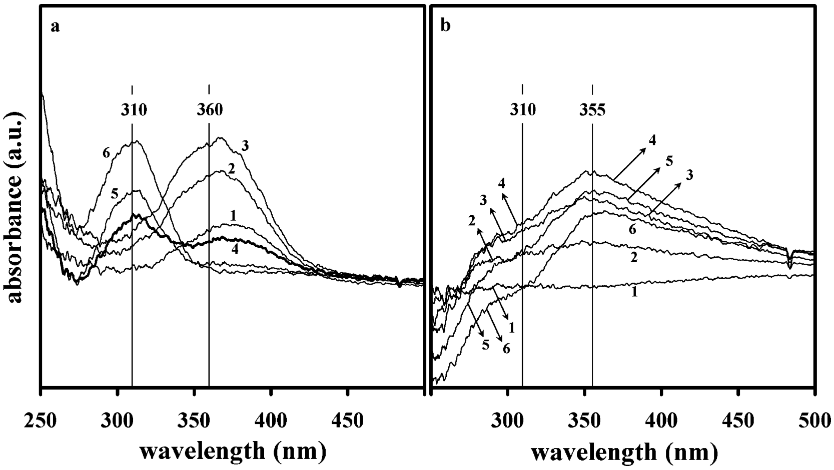

Fig. 5. In situ DR UV–vis difference spectra of Ag/Al_2O_3 catalyst at 150 °C upon nitrate formation in presence of 500 ppm NO_2, 6% O_2 and 3% H_2O (a) and during subsequent elimination of the nitrates in a gas stream of 1000 ppm NO, 6% O_2 and 3% H_2O (b). Timing of spectra in (a): 1 (5 min), 2 (25 min), 3 (45 min), 4 (135 min), 5 (145 min), and 6 (255 min); in (b): 1 (10 min), 2 (30 min), 3 (50 min), 4 (90 min), 5 (150 min), and 6 (230 min).

(Fig. 4a) displayed a burst of NO_x followed by tailing NO_x release. The sample saturated with nitrates in the presence of 500 ppm NO and 500 ppm NO_2 showed a much more gradual NO_x release (Fig. 4b). The experiment demonstrates that the kinetics of the reaction of silver nitrate with NO is dependent on the conditions under which the silver nitrate was formed.

Nitrate formation was investigated on the alumina support. The NO_x adsorption capacity of the alumina, pretreated at 400 °C in a gas stream with 6% oxygen and 12% water when contacted with 500 ppm NO_2 was 614 $\mu mol\,g^{-1}$ at 150 °C (Table 1, column 4). This value is higher than on the Ag/Al_2O_3 catalyst (383 $\mu mol\,g^{-1}$) but can be explained by the significant difference in specific surface area, viz. 358 $m^2\,g^{-1}$ for the alumina compared to 187 $m^2\,g^{-1}$ for Ag/Al_2O_3. This NO_x adsorption experiment caused a reduction of the B.E.T. specific surface area to 289 $m^2\,g^{-1}$ for Al_2O_3 and 111 $m^2\,g^{-1}$ Ag/Al_2O_3. The nitrates were eliminated in the presence of 1000 ppm NO, 6% O_2 and 12% H_2O. NO_x desorption occurred in two steps, similar to the Ag/Al_2O_3 catalyst (Table 1). The present results suggest that the addition of silver to the alumina support alters the surface chemistry so that aluminum nitrates that react with NO at low temperatures are no longer present. A quantity of ca. 383 $\mu mol\,g^{-1}$ of nitrate was decomposed at 150 °C (Step 1) and 233 $\mu mol\,g^{-1}$ upon heating to 400 °C. The $NO_{2\,\text{release}}/NO_{\text{react}}$ ratio was ca. 3.0 reflecting the stoichiometry of the reaction of nitrate with NO into NO_2.

3.3. Spectroscopic investigations

The formation of nitrates on Ag/Al_2O_3 was monitored by means of in situ DR UV–vis spectroscopy at 150 °C. Pretreated catalyst was contacted with a gas stream of 500 ppm NO_2 (Fig. 5a) next to 6% O_2 and 3% H_2O. The spectrum of pretreated catalyst was subtracted from all spectra in order to obtain difference spectra. First, a relatively broad band centered around 360 nm grew in the first 45 min (spectra 1–3). Subsequently, this band eroded while a new band around 310 nm appeared (spectra 4–6). The spectra displayed an isosbestic point around 340 nm, meaning that the species responsible for the band around 360 nm is converted into the species that absorbs around 310 nm. From the volumetric experiments already discussed, it was derived that under these conditions all silver of the catalyst is finally converted into silver nitrate. Therefore, the band at 310 nm in the spectrum of nitrated catalyst is ascribed to silver nitrate. The assignment of the band at 360 nm is less evident. It is speculated that it is linked with coordination of Ag(I) with NO_2 preceding the formation of nitrate, which would explain its transient appearance.

The nitrates generated in the experiment of Fig. 5a were eliminated in a gas stream of 1000 ppm NO, 6% O_2 and 3% H_2O in helium. The DR UV–vis spectrum of the nitrate saturated sample was subtracted from the sequentially taken spectra 1–6 (Fig. 5b). A broad absorbance in the wavelength region 270–500 nm increased gradually upon desorption. In the early spectra 2–4, absorbance was gained with time mainly around 310 and 355 nm, while the absorbance below 270 nm decreased. After 90 min (spectrum 4) the absorbance around 310 nm decreased again. Finally in spectrum 6 only absorption around 355 nm remained. UV absorption below 270 nm is attributed to Ag(I) cations [32]. Absorption in a broad UV spectral range encompassing maxima around 305 and 370 nm was previously observed on Ag/Al_2O_3 catalyst treated in the presence of oxygen and hydrogen and ascribed to silver clusters [22], the wavelength of absorption increasing with increasing cluster size [32]. The volumetric experiments and the $NO_{2\,\text{release}}/NO_{\text{react}}$ ratios (Table 1) revealed that elimination of nitrates through reaction with NO leads to a combination of Ag(0) and Ag(I). In view of this conclusion and spectroscopic literature data [5,15,22, 32], the absorbances around 310 and 355 nm (Fig. 5b) are

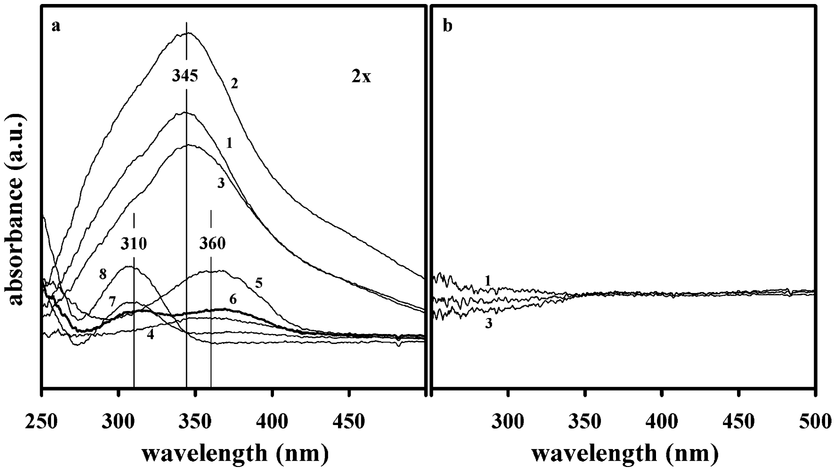

Fig. 6. In situ DR UV–vis difference spectra of Ag/Al_2O_3 catalyst at 150 °C upon nitrate formation in presence of 500 ppm NO_2, 1000 ppm NO, 6% O_2 and 3% H_2O (a) and during subsequent elimination of the nitrates in a gas stream of 1000 ppm NO, 6% O_2 and 3% H_2O (b). Timing of spectra in (a): 1 (5 min), 2 (13 min), 3 (30 min), 4 (48 min), 5 (109 min), 6 (195 min), 7 (205 min), and 8 (365 min); in (b) 1 (15 min), 2 (55 min), and 3 (140 min).

assigned to partially charged and metallic Ag clusters, respectively.

Following these assignments of the UV absorptions, both silver nitrate and partially charged silver clusters absorb UV light around 310 nm. It explains the evolution of the spectra in Fig. 5b, whereby the 310 nm absorbance first grows due to formation of charged silver clusters and decreases later on upon further elimination of the silver nitrate and partially charged clusters.

A similar in situ DR UV–vis study was performed during nitrate formation in the presence of a gas mixture in which NO_x was present as a mixture of 500 ppm NO_2 and 1000 ppm NO (Fig. 6a). An intense absorption around 345 nm grew quickly after contacting pretreated catalyst with the NO_x containing gas (spectrum 1). Note the difference with the experiment of Fig. 5a in absence of NO, where the temporary UV absorption was at 360 nm. After 13 minutes (spectrum 2) the absorbance at 345 nm was already decreased. After 48 min it completely disappeared (spectrum 4). Absorption around 360 nm appeared at intermediate times (spectrum 5 and 6). In the final spectra 7 and 8 the absorbance peaked around 310 nm. This sequence of absorptions at 360 and 310 nm was similar to the experiment in absence of NO (Fig. 5a).

The origin of the band at 345 nm in Fig. 6a is unknown. Given its quick formation, it should be linked with a primary product from chemisorption of NO_2 together with NO. A speculative interpretation is that Ag(I) coordinated to N_2O_3 molecule formed out of NO and NO_2 could be responsible for this UV absorption.

In situ DR UV–vis spectra were recorded during elimination of the nitrates from the catalyst of Fig. 6a under a gas stream of 1000 ppm NO (Fig. 6b), oxygen and water adopting the same procedure as in Fig. 5b. Besides an intensity decrease around 270 nm, assigned to a diminishing of Ag(I) cations, the spectrum surprisingly changed very little during the nitrate elimination reaction. From the volumetric experiments (Table 1, column 3, Step 1) and the $NO_{2\,\mathrm{release}}/NO_{\mathrm{react}}$ value of 2.6 it is known that silver nitrate formed on Ag/Al_2O_3 catalyst in the presence of a mixture of NO_2 and NO reacts with NO into Ag(0) and Ag(I) species. The absence of significant absorbance in the difference spectra of Fig. 6b is interpreted as a formation of very small metallic silver particles, absorbing in the spectral range of silver nitrate and charged silver clusters, i.e. around 310 nm, so that the decreasing UV absorption owing to silver nitrate is compensated by increasing absorption of charged and metallic Ag clusters. The decreased aggregation of Ag(0) in this regenerated sample must originate from a particularly high dispersion of silver nitrate on the catalyst when formed in the presence of a mixture of NO_2 and NO. This interpretation is supported by the observation that the elimination of nitrates from catalyst nitrated in the presence of 500 ppm NO and 500 ppm NO_2 (Fig. 4b) was much slower than from catalyst nitrated in the presence of 500 ppm NO_2 only (Fig. 4a). It is to be expected that during nitrate formation out of NO_2 the presence of 500 ppm NO suppresses the development of larger silver nitrate particles given the dynamics of formation (Eq. (1)) and disproportionation (Eqs. (5) and (6)) of the silver nitrate.

3.4. Volumetric NO_x adsorption experiments in the presence of hydrogen

Pretreated Ag/Al_2O_3 catalyst was contacted at 150 °C with a gas mixture comprising 1000 ppm NO, 3500 ppm H_2, 6% O_2 and 12% H_2O. The evolution of NO_x concentration in the reactor outlet was registered (Fig. 7). In this experiment in the presence of hydrogen, Ag/Al_2O_3 did adsorb NO. The NO_x adsorption capacity was estimated at ca. 181 $\mu mol\,g^{-1}$. Formation of NO_2 was detected showing that the catalyst displayed NO into NO_2 oxidation activity. Thus, whereas in the absence of hydrogen, Ag/Al_2O_3 catalyst is inert to NO (cf. Section 3.2), in the presence of 3500 ppm hydrogen it displays reactive adsorption.

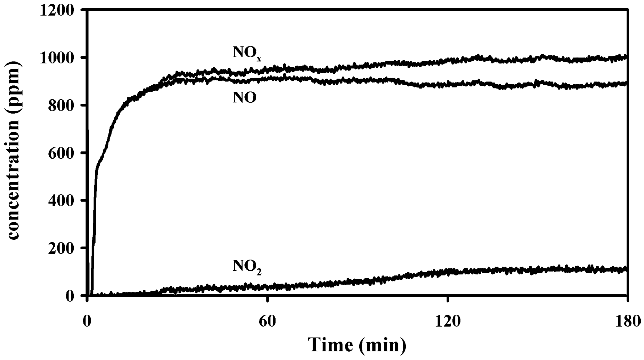

Fig. 7. Evolution of NO, NO_2, and NO_x concentration in outlet of Ag/Al_2O_3 catalyst bed contacted at 150 °C with a gas mixture composed of 1000 ppm NO, 3500 ppm H_2, 6% O_2 and 12% H_2O in helium.

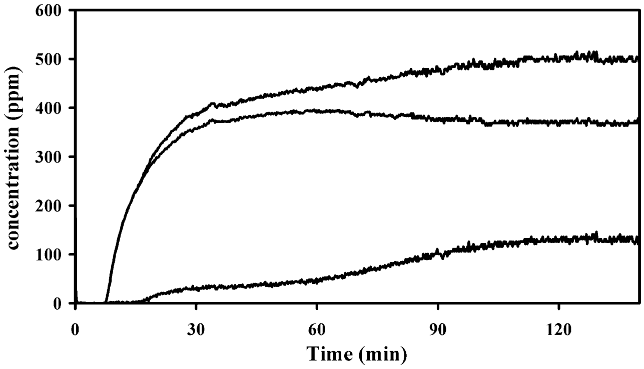

Fig. 8. Evolution of NO, NO_2, and NO_x concentration in outlet of Ag/Al_2O_3 catalyst bed contacted at 150 °C with a gas mixture composed of 500 ppm NO_2, 3500 ppm H_2, 6% O_2 and 12% H_2O in helium.

In a further experiment, the usual gas mixture spiked with 500 ppm NO_2 and 3500 ppm hydrogen was passed over the reactor loaded with oxidized Ag/Al_2O_3 catalyst at 150 °C and the outlet NO_x concentration monitored (Fig. 8). During the first 15 min the NO_x fed to the reactor was entirely adsorbed. After 10 min, NO release set in. Saturation was reached after ca. 120 min. There was substantial catalytic reduction of NO_2 into NO by reaction with hydrogen detected after saturation of the catalyst with NO_x. The NO_x adsorption capacity was ca. 211 $\mu mol\,g^{-1}$. This is less than the NO_x adsorption capacity under the same conditions in the absence of hydrogen, viz. 383 $\mu mol\,g^{-1}$ (Table 1). In the presence of hydrogen, adsorption of NO_2 does not instantaneously give rise to NO evolvement (Fig. 8) as was observed in the absence of hydrogen (Fig. 2), indicating that the NO_x adsorption chemistry is different. The presence of silver nitrate was probed by reacting saturated catalyst with NO gas mixture at 150 °C. Upon contacting the catalyst with NO holding gas, the outlet NO_x concentration rose only slightly above the inlet value (Fig. 4c). The silver nitrate content estimated from the NO_x evolving from the catalyst was estimated at ca. 94 $\mu mol\,g^{-1}$, corresponding to about half of the silver content (185 $\mu mol\,g^{-1}$). It is concluded that a substantial fraction of the silver is not converted into nitrate when contacting the catalyst with gas mixture of NO_2 and hydrogen. The slow reaction of silver nitrate with NO (Fig. 4c) suggests that the silver nitrate is very well dispersed. The assignment of NO_x release to silver nitrate in this experiment must be made, however, with caution because silver nitrate could be formed out of Ag(0) and aluminum nitrate during the NO reaction itself. Metallic silver clusters are known to oxidize readily upon exposure to a stream with oxygen and NO [22].

Ag/Al_2O_3 catalyst was contacted at 150 °C with a gas stream comprising 500 ppm NO_2, 3500 ppm H_2, 6% O_2 and 12% H_2O. When saturation noticed by outlet NO_x concentration regaining the inlet value was reached, the hydrogen supply was closed and the NO_x adsorption continued. The NO_x capacity increased from ca. 211 to 383 $\mu mol\,g^{-1}$ by removing hydrogen from the gas stream. This final capacity of ca. 383 $\mu mol\,g^{-1}$ is very similar to the capacity in absence of hydrogen (Table 1). The gain in NO_x adsorption capacity by ca. 172 $\mu mol\,g^{-1}$ corresponds within experimental error to the silver content of the catalyst. This experiment revealed that in the presence of hydrogen, aluminum nitrate is selectively formed while silver is mostly in reduced state. The reactivity of reduced silver toward NO_2 was verified in an experiment in which catalyst sample was first reduced in hydrogen and then contacted with a gas mixture of 500 ppm NO_2, 6% O_2, and 12% H_2O at 200 °C. The NO_x adsorption capacity was ca. 262 $\mu mol\,g^{-1}$, similar to the 265 $\mu mol\,g^{-1}$ determined on oxidized catalyst (Table 1), confirming the formation of silver nitrate next to aluminum nitrate.

The following experimental observation further substantiates the instability of silver nitrate of Ag/Al_2O_3 catalyst in the presence of minute concentrations of hydrogen. Ag/Al_2O_3 catalyst was saturated with nitrates at 200 °C in the presence of 500 ppm NO_2, 6% O_2 and 12% H_2O. Flushing with a gas stream of 3500 ppm H_2 and 12% H_2O immediately gave rise to NO_2 evolvement the quantity of which matching with the silver nitrate content.

All these experiments corroborate the existence of Ag(0) on the Ag/Al_2O_3 catalyst in the presence of NO_x and hydrogen. The catalytic role of reduced silver in aluminum nitrate formation out of NO_2 in the presence of hydrogen can be explained as follows:

$$Ag_2O + H_2 \rightleftharpoons 2Ag(0) + H_2O, \quad (8)$$

$$Ag(0) + NO_2 \rightleftharpoons Ag(NO_2), \quad (9)$$

$$Ag(NO_2) + NO_2 \rightleftharpoons Ag(NO_3) + NO. \quad (10)$$

Given that there is a period of total NO_2 adsorption without release of NO (Fig. 8), it is suggested that disproportionation of silver nitrite into silver nitrate is a slow step. Silver nitrate can be reduced by hydrogen:

$$Ag(NO_3) + H_2 \rightleftharpoons Ag(0) + NO_2 + H_2O \quad (11)$$

and

$$6Ag(NO_3) + Al_2O_3 \rightleftharpoons 3Ag_2O + 2Al(NO_3)_3. \quad (12)$$

In the presence of hydrogen, Ag(0) impedes the nitric acid formation (Eq. (1)) by trapping the NO_2 and formation of

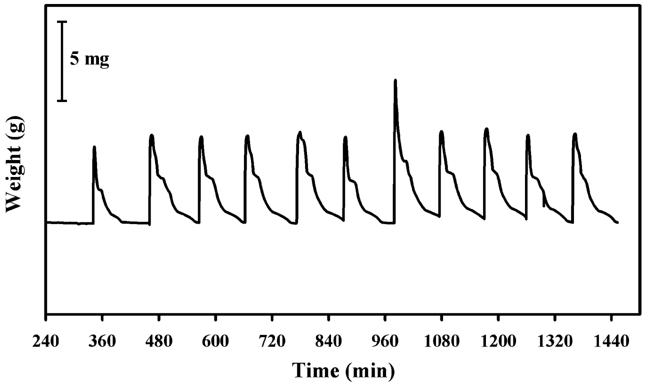

Fig. 9. Weight variation of Ag/Al_2O_3 sample (210 mg) exposed to helium containing 5% H_2O and 1% O_2 at 100 °C.

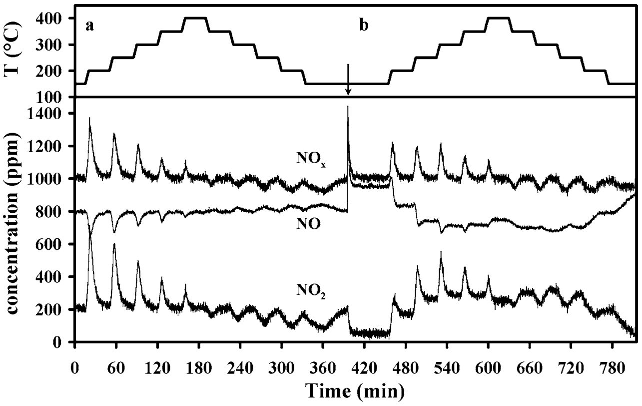

Fig. 10. Monitoring of NO, NO_2, and NO_x concentration in outlet of Ag/Al_2O_3 catalyst bed subjected to (a) stepped temperature profile and contacted with a gas mixture composed of 200 ppm NO_2, 800 ppm NO 6% O_2 and 12% H_2O. In part (b) starting at the arrow 3500 ppm H_2 was added to the gas stream.

silver nitrite. After saturation of the support with nitrate (Eq. (12)), silver is involved in a redox cycle constituted of Eqs. (9), (10), and (11) the net result of which is given by Eq. (13).

$$NO_2 + H_2 \rightleftharpoons NO + H_2O. \tag{13}$$

At 100 °C, hydrogen has hardly an influence on nitrate formation capacity (Table 1, column 2, compared to column 5). At 100 °C, the Ag/Al_2O_3 surface is covered by many layers of physisorbed water molecules, which drastically limit the adsorption of hydrogen. Nitrate formation proceeds through nitric acid formation (Eq. (1)).

Pretreated Ag/Al_2O_3 catalyst was mounted in an ultra high precision magnetic suspension balance and contacted at 100 °C with a gas stream of helium with 5% H_2O and 1% O_2. The catalyst weight was not stable and oscillated between two levels (Fig. 9) representing a weight difference of ca. 3 wt%. At 200 °C, the weight oscillation was smaller. Alumina support did not reveal this phenomenon. The silver concentration of the catalyst is too small to explain these weight changes. Hydroxylation and dehydroxylation of the alumina catalyzed by silver is the most obvious explanation. The behavior shows that the Ag/Al_2O_3 surface is very reactive and that silver influences the whole surface. The transfer of nitrate from silver to the alumina support in the presence of hydrogen (Eq. (12)) fits into this picture.

3.5. Impact of hydrogen on catalytic behavior in SCR of NO_x

In automotive applications of Ag/Al_2O_3 catalyst, temperature varies significantly. The impact of temperature changes was evaluated in NO_x chemisorption experiments in the presence and absence of hydrogen. After pretreatment of Ag/Al_2O_3 at 400 °C in oxidizing atmosphere, the catalyst was exposed to a gas feed consisting of 200 ppm NO_2, 800 ppm NO, 6% O_2 and 12% H_2O (Fig. 10). Temperature steps from 150 to 400 °C and back to 150 °C were applied and the outlet NO, NO_2, and NO_x concentrations recorded. At the start of the experiment the catalyst is saturated with nitrates detected by adsorption of NO_2 and release of NO. When the temperature is increased, NO_2 evolves from the catalyst by elimination of nitrates through reaction with NO. When the catalyst temperature is decreased again, nitrates are formed by adsorption of NO_2 and release of NO. On the temperature plateaus, NO_2 and NO levels regain the inlet values showing that there is little NO oxidation activity owing to the lack of Ag(0). The molar ratio of $NO_{2\,\mathrm{react}}/NO_{\mathrm{release}}$ and of $NO_{2\,\mathrm{release}}/NO_{\mathrm{react}}$ were close to 3. After the catalyst regained 150 °C, hydrogen was added to the gas feed. There was immediately a release of some NO and catalytic reduction of NO_2 with hydrogen into NO revealing the formation of some Ag(0). In each temperature step, there is release of NO_x as NO_2. In the presence of hydrogen the NO consumption, detected as negative peaks in the NO concentration trace, is smaller than in the absence of it, probably because of reductions of NO_2 into NO during the NO_2 release peaks. On the temperature plateaus in the presence of hydrogen, the catalyst oxidizes NO into NO_2 over Ag(0).

In literature, the poor catalytic activity of Ag/Al_2O_3 at temperatures below 250 °C was ascribed to inhibition of active sites by adsorbed nitrates [5,13,24,29]. In the present work the quantitative transformation of all silver into silver nitrate under such conditions is demonstrated (Table 1). The promotion of the *SCR of NO_x* activity of Ag/Al_2O_3 by H_2 can be explained by formation of Ag(0) even in the presence of 6% oxygen and 500 ppm NO_2 and 12% H_2O. This Ag(0) can be responsible for the activation of the hydrocarbons through partial oxidation, proposed to be an essential reaction step in *HC-SCR of NO_x*.

4. Conclusions

In the absence of reducing agent, a significant nitrate formation on Ag/Al_2O_3 catalyst. The nitrate formation proceeds through the nitric acid formation reaction out of NO_2 and water as revealed by the formation of 1 NO molecule per three NO_2 molecules reacted with the catalyst. The formation of silver and aluminum nitrates can be quantified based on their reactivity toward NO at 150 and above 200 °C, respectively. In NO_2 containing gas streams, at temperatures below 200 °C all silver is transformed into silver nitrate. This observation supports the suggestion in literature that the low temperature poisoning of the *SCR of* NO_x activity is due to nitrate formation on silver. Silver nitrate of the catalyst reacts with NO according to two different reaction pathways leading to a combination of Ag(I) and Ag(0) species. Aluminum nitrate formation on the support decreases with increasing temperature.

The silver nitrate formation can be monitored with in situ DR UV–vis spectroscopy. UV absorption around 310 nm is ascribed to silver nitrate. Reaction of nitrated catalyst with NO leads to formation of partially charged and metallic silver clusters absorbing around 310 and 355 nm, respectively. In situ DR UV–vis spectroscopy and nitrate elimination kinetics reveal that the dispersion of silver nitrate formed upon reaction with NO_2 is higher in the presence of NO than in its absence.

In the presence of hydrogen, nitrate formation proceeds according to a mechanism in which silver nitrite formed upon reaction of NO_2 with Ag(0) is oxidized by NO_2. Nitrates are transferred from silver to the support. Ag(0) is regenerated by reduction of silver nitrate with hydrogen. In the absence of hydrogen, below 200 °C all silver is present as silver nitrate. In the presence of minute concentrations of hydrogen such as 3500 ppm H_2 next to 6% O_2, a significant fraction of the silver is reduced to the metallic state. It explains the boosting of catalytic activity of *SCR of* NO_x by hydrogen at low temperatures.

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