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Ammonia blocking of the “Fast SCR” reactivity over a commercial Fe-zeolite catalyst for Diesel exhaust aftertreatment

Antonio Grossale, Isabella Nova, Enrico Tronconi *

Dipartimento di Energia, Laboratorio di Catalisi e Processi Catalitici, Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133 Milano, Italy

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ABSTRACT

The ammonia blocking effect on the Fast SCR catalytic mechanism at low temperature has been studied by means of dedicated transient reactivity runs performed over a state-of-the-art commercial Fe-zeolite catalyst. We show that the reduction of surface nitrates by NO is the key step in the mechanism, and is active already at 50 °C. However, in the presence of ammonia the reaction between NO and nitrates is stopped, and proceeds only on raising the temperature up to 140–160 °C, which thus represents an intrinsic lower bound to the Fast SCR activity. Evidence is provided that such a blocking effect is associated with a strong interaction between ammonia and surface nitrates, which prevents nitrates from reacting with NO: only upon increasing the temperature or decreasing the NH_3 concentration nitrates are released due to dissociation of the ammonia–nitrate complex. The present data thus provide evidence that the blocking effect of NH_3 on the Fast SCR activity at low temperature occurs not because of the ammonia competitive chemisorption on the catalytic sites, but because ammonia captures a key intermediate in an unreactive form.

1. Introduction

The selective catalytic reduction (SCR) technology is well established and used worldwide to control the emissions of NO_x from stationary sources [1,2]: it can be broadly described as passing a hot exhaust gas over a catalyst in the presence of nitrogenous reductants, such as ammonia or urea, according to the so called Standard SCR reaction (1)

$$2NH_3 + 2NO + 1/2\,O_2 \rightarrow 2N_2 + 3H_2O \tag{1}$$

SCR is also currently employed to reduce NO_x contained in the exhaust gases of internal combustion engines operated with excess air, such as Diesel engines.

One problem of SCR systems for vehicles is the poor activity at low temperatures where most of the NO_x are produced during, e.g. cold start-up and on short travelling distances. A method to increase the efficiency of NO_x removal by SCR when the exhaust gas temperature is low is to increase the temperature of the exhaust gas and/or of the SCR catalyst. In the case of mobile applications, the method mostly used to enhance the DeNOx activity of SCR catalysts at low temperature is to increase the NO_2/NO molar ratio (NO_2 accounts only for few percent of the total NO_x in the exhaust gases), thus promoting the occurrence of the Fast SCR reaction (2) [3].

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \tag{2}$$

This has been realized in practice by installing on board aftertreatment systems that incorporate an oxidation catalyst to convert at least a portion of NO to NO_2 upstream of the SCR converter, the oxidation catalyst typically consisting of a Pt catalyst carried on a flow-through honeycomb support: in this case considerable improvements in NO_x conversion have been observed.

The SCR technology was first commercialized on heavy duty vehicles in 2005 [4], based on the use of extruded honeycomb monolith catalysts consisting of $V_2O_5/WO_3–TiO_2$. However, recently zeolite-based catalysts promoted by transition metals such as Fe and Cu are being considered due to the low stability of titania at high temperatures, and to the tightening of the NO_x emission limits for both HD and LD vehicles, which calls for higher activity at low temperatures.

Several papers can be found in the literature which analyze the reactivity, the mechanism, and the kinetics of the Fast $NO/NO_2–NH_3$ SCR reaction [5–19]. In a previous study of a Fe-zeolite catalyst [12], we proposed that the Fast SCR reaction at low temperature proceeds according to a mechanism which comprises: NO_2 disproportionation to form nitrate ad-species\nitric acid and nitrite ad-species\nitrous acid (3), the reaction between nitrate ad-species\nitric acid and NO to form nitrite ad-species\nitrous acid and NO_2 (4), the reaction of ammonia with nitrite ad-species\nitrous acid to give nitrogen and water via ammonium nitrite decomposition (5), and the reaction of ammonia with nitrate ad-species\nitric acid to give ammonium nitrate (6) [12]:

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* Corresponding author. Fax: +39 02 2399 3318.
E-mail address: enrico.tronconi@polimi.it (E. Tronconi).

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$$2NO_2 + H_2O \leftrightarrow HNO_3 + HONO \quad (3)$$

$$HNO_3 + NO \leftrightarrow NO_2 + HONO \quad (4)$$

$$NH_3 + HONO \rightarrow [NH_4NO_2] \rightarrow N_2 + 2H_2O \quad (5)$$

$$NH_3 + HNO_3 \leftrightarrow NH_4NO_3 \quad (6)$$

Notice that, for the sake of simplicity, reactions are herein written in terms of molecular species: reaction steps (3)–(6) actually involve surface nitrites and nitrates, which are, however, indicated as HONO and HNO_3, respectively, above as well as in the rest of the present paper. The spectroscopic and mechanistic work of Sachtler's group has provided important insight into the nature of the surface species involved in NH_3–SCR over Fe-ZSM-5 [20,21]. A relevant summary is also provided in a recent review [19].

According to (3)–(6), thus, the Fast SCR stoichiometry (2) results from a combination of the crucial reaction steps above, in which NO_2 acts both as a reactant (3) and as a product (4). In fact NO reacts with surface nitrates (4) that are formed by NO_2 disproportion (3), producing nitrites and NO_2. Nitrites react with ammonia to form ammonium nitrite which decomposes to N_2 and H_2O (6). NO_2 previously formed by (4) could form additional nitrates/nitrites by the disproportionation reaction (3) [12]. In such a cycle the key reaction is the one between NO and nitrates, step (4).

Moreover, data reported in a previous study [12] pointed out that at 150–170 °C ammonia can strongly inhibit reaction (4); this effect represents an intrinsic limitation of the low temperature activity of the Fast SCR reaction. The ammonia blocking effect was explained by considering that ammonia influences the equilibrium of reaction (6): when the equilibrium is shifted to the right-hand side ammonium nitrate is formed, and this prevents nitric acid/nitrates, i.e. the true reactive species, from reacting with NO.

In the present paper we analyze in more detail the blocking action of ammonia on the rate determining ammonium nitrate + NO reaction (4) of the "Fast SCR" mechanism over another commercial state-of-the-art Fe-zeolite catalyst, using dynamic methods.

2. Experimental

The experimental work was performed over a commercial catalyst originally supplied by Daimler in the form of a cordierite honeycomb monolith (400 cpsi-6.5 mils) washcoated with a Fe-Beta zeolite (Si/Al = 24, Fe/Al = 1.5, BET area = 227 m^2/g) prepared by ion-exchange. The total washcoat load was around 160 g per liter of monolith structure.

A sample of 80 mg of catalyst (crushed to powder and sieved to 140–200 mesh, to avoid mass transfer limitations) diluted with 80 mg of quartz powder was loaded in a flow-microreactor consisting of a quartz tube (6 mm i.d.) placed in an electrical furnace. A *K*-type thermocouple immersed in the catalyst bed was used to monitor and control the reaction temperature. Mass flow controllers (Brooks Instruments) were used to dose He, NH_3, NO, NO_2, and O_2 in the gaseous feed stream, while water vapor was added via a saturator operated at controlled temperature. All the lines before and after the reactor were heated to 200 °C to prevent H_2O condensation and NH_4NO_3 deposition. The species concentrations in the outlet stream were continuously monitored by a quadrupole mass spectrometer (Balzer QMS 200) and a UV analyzer (ABB–LIMAS 11 HV) in parallel. Helium was used as carrier gas to enable evaluation of N-balances at steady state. More experimental details are available elsewhere [9,11,12].

Catalyst conditioning consisted in a temperature ramp of 10 K/min up to 600 °C in 2% O_2 v/v + 10% H_2O, followed by hold at 600 °C for 2 h. All tests were carried out at 71 cm^3/min (STP), corresponding to GHSV = 32,000 h^{-1} if referred to a monolith catalyst.

Two different kinds of transient experiments were performed. In transient response method (TRM) runs the reactor was kept at constant temperature under a flow of He + 1% H_2O, and step changes (e.g., 0 → 1000 → 0 ppm or 0 → 500 → 0 ppm) of NH_3 or NO or NO_2 feed concentrations were imposed. At the end of the dynamic test a temperature ramp (20 K/min, T_{end} = 450 °C) in He and H_2O (1% v/v) was run to study desorption and decomposition of adsorbed surface species. As opposite, in temperature programmed surface reaction (TPSR) runs a first phase similar to the TRM tests (adsorption of one or more species) was performed, followed by a temperature ramp (20 K/min, T_{end} = 450 °C) where one or more other gaseous species were continuously fed to the reactor. These experiments allowed to study the reactivity of gaseous components with surface adsorbed species.

A few additional experiments over a different Fe-zeolite [12] were carried out to confirm the NH_3 blocking effect on the "Fast SCR" reaction. These runs were performed at 150 and 170 °C: after a first phase where NH_3, NO, and NO_2 (1000:500:500 ppm) were fed simultaneously to the reactor, the dynamic behavior of the reacting system upon $NH_3\backslash NO_2$ shut off was investigated.

Since the purpose of this work was to study the "Fast SCR" reaction (2) and its mechanism, all the runs were performed in the absence of O_2 so as to rule out any contribution of the standard SCR reaction (1).

3. Results and discussion

3.1. Reaction between nitrates and NO: ammonia blocking effect

To study the key reaction step (4) we analyze the reactivity of gaseous NO at low temperatures in the presence of nitrate species preadsorbed on the catalyst surface (Fig. 1A and B). At 50 °C, 1000 ppm of NO_2 is first fed to the catalyst in the presence of H_2O (1% v/v) and without O_2 to form and store nitrates onto the catalyst surface [6,8,12–14,22]; then, after NO_2 is shut off, 1000 ppm of NO is added to the reactor feed stream in order to study the reactivity of nitric oxide with surface nitrates at 50 °C (Fig. 1A). Finally, a temperature ramp, still in the presence of gaseous NO, is performed to study the temperature effect (Fig. 1B).

Fig. 1A confirms that feeding NO_2 at low temperature to the Fe-zeolite catalyst results in the formation of surface nitrates: upon addition to the reactor, in fact, the NO_2 outlet concentration trace shows a dead time during which NO is produced (350–360 ppm). As well known in the literature [12–23], NO_2 consumption and the corresponding NO evolution are explained by formation of nitrates on catalyst surface, according to NO_2 disproportionation:

$$2NO_2 + H_2O \leftrightarrow HNO_3 + HONO \quad (3)$$

$$NO_2 + HONO \leftrightarrow NO + HNO_3 \quad (4a = 4\text{reverse})$$

whose addition yields

$$3NO_2 + H_2O \leftrightarrow 2HNO_3 + NO \quad (7)$$

Indeed, a quantitative analysis confirms that the molar ratio between evolved NO and converted NO_2 is close to 1/3, as expected from the global reaction (7).

In view of the very low temperature, and of the high H_2O feed content, it is likely that liquid water was filling the catalyst pores during the NO_2 storage transient. When the NO_2 storage experiment was replicated at 200 °C, however, the same behavior was observed, still involving evolution of NO in 1/3 molar ratio with adsorbed NO_2. Thus, H_2O is not essential and the same NO_2 adsorption chemistry applies both in the presence and in the absence of liquid H_2O on the zeolite. This conclusion was further confirmed by NO_2 adsorption–desorption runs over a different Cu-zeolite, that were performed both including and excluding H_2O from the feed stream. The same data also suggest that surface reactions, rather then homogeneous ones, prevail in NO_2 adsorption.

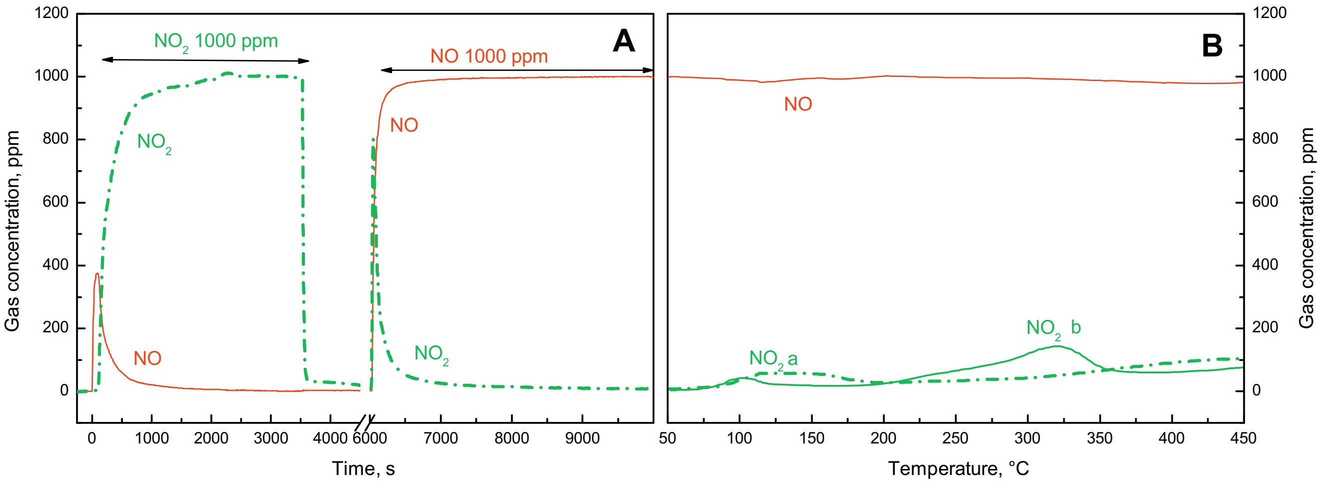

Fig. 1. (A) TRM at 50 °C: NO_2 adsorption (1000 ppm) followed by nitrates + NO (1000 ppm) reaction in a flow of $H_2O = 1\%$, $O_2 = 0\%$, He balance; (B) TPSR: T-ramp at 20 K/min while flowing NO (1000 ppm), $H_2O = 1\%$, $O_2 = 0\%$, He balance. Curve b in (B) is the NO_2 trace from a TPD run (thermal decomposition in inert atmosphere of nitrates formed by NO_2 adsorption at 50 °C, T-ramp at 20 K/min).

In the second part of the run in Fig. 1A, at $t = 6000$ s NO is fed onto a catalyst whose surface is saturated by nitrates. In spite of the low temperature (50 °C) the catalyst shows a strong activity: NO is initially converted while NO_2 formation (800 ppm) is evident.

This behavior could be explained both by reaction (4) and by the reverse of reaction (7), i.e. reaction (7a)

$$2HNO_3 + NO \leftrightarrow 3NO_2 + H_2O \tag{7a}$$

However, the ratio between the integral production of NO_2 and NO consumption calculated from the experimental result is close to 2, this value being in agreement with none of the reactions above between NO and nitrates, i.e. neither with reaction (4), for which the expected ratio should be 1, nor with reaction (7a), for which the ratio should be 3.

Thus, both reactions are probably occurring simultaneously: nitrates present on the catalyst surface react with NO producing NO_2 and nitrites according to (4), and then only part of such nitrites are further oxidized by other nitrates according to (3 reverse).

In Fig. 1B the subsequent TPSR ramp is shown. In the range 100–175 °C a small peak of NO_2 (curve a) is evident while NO shows no reactivity in the whole investigated T-range.

For comparison purposes the NO_2 profile (curve b) obtained performing a TPD (thermal decomposition in inert atmosphere of nitrates formed by NO_2 adsorption at 50 °C) is also displayed in Fig. 1B. The comparison points out that during the present TPSR run (curve a) the peak at 320 °C, visible in the TPD run (curve b) and associated with nitrates decomposition [12,18,24], is not present; this indicates that the most stable nitrate species formed during NO_2 adsorption were removed by reaction with NO already at 50 °C (Fig. 1A), and thus only small quantities of weakly adsorbed NO_2, likely related to the liquid water in the zeolite pores, evolve during the following T-ramp.

In conclusions, the experiment in Fig. 1 shows that the activity of NO in reducing surface nitrates is very strong already at low temperature (50 °C), even if NO was unable to deplete all of the NOx stored on the catalyst surface.

Apparently, such a strong NO reactivity toward nitrates at 50 °C is not consistent with the hypothesis that considers reaction (4) the rate determining step of the Fast SCR mechanism. Previous results [12,18] showed in fact that the Fast SCR activity starts only around 150–160 °C, while, as evident from Fig. 1A, the NO + HNO_3 reaction (4) is active at 50 °C.

However, it should be noticed that ammonia is present in the Fast SCR reacting system, while NO oxidation by nitrates at 50 °C (Fig. 1A) was performed without ammonia in the feed stream. Indeed, it is known already from the literature [12,15,18] that NH_3 plays a strong blocking effect on the Fast SCR reaction (2), an effect that was found critical at low temperature.

To study these aspects a new test was performed (Fig. 2A and B): the experiment was identical to that reported in Fig. 1, but for the fact that the reactivity of NO toward nitrate adsorbed species was analyzed in the presence of gaseous ammonia.

Fig. 2A shows the NO_2 addition (1000 ppm) at 50 °C over a clean catalyst, and the results are very similar to those shown in Fig. 1A: NO_2 is consumed with simultaneous NO evolution, in line with the 1:3 stoichiometry expected from reaction (7). Then, immediately before $t = 6500$ s 1000 ppm of ammonia are added to the feed flow: no reactions are observed, and after a transient during which ammonia is adsorbed onto the catalyst the ammonia outlet concentration reaches its feed value.

Afterwards, at $t = 8000$ s NO is added to the reactor feed and its outlet concentration quickly recovers the inlet value, indicating that no reaction occurs as well. So, as opposite to the case of Fig. 1A, where NO reduced nitrates present onto the catalyst surface, in a TRM test performed at the same temperature in the presence of ammonia (Fig. 2A), NO does not react with nitrate adspecies. This is a clear proof that ammonia blocks the reaction between NO and nitrates at low temperature over the present Fe-Beta zeolite. It should be further emphasized that the NH_3 inhibition of the nitrates reactivity with NO had been observed previously over Fe-ZSM-5 [11] and discussed in relation to NH_4NO_3 formation over a Ba Na-Y zeolite [14]: it is apparently a general feature of the SCR chemistry over zeolite catalysts.

Additional information can be obtained analyzing the following TPSR part of the run (Fig. 2B): after a first strong NH_3 desorption due to the initial heating, starting at 140–160 °C NO is consumed and a simultaneous production of N_2 is observed. NO conversion reaches a maximum value close to 80% at 210 °C with a corresponding peak of 1160 ppm of nitrogen production. In addition, ammonia also shows a conversion peak. After decreasing, at T > 300°C the NO and NH_3 conversions start again to grow slowly with temperature, accompanied by a limited production of nitrogen.

Minor amounts of N_2O and NO_2 are produced as well during the T-ramp, in the range 175–250 °C.

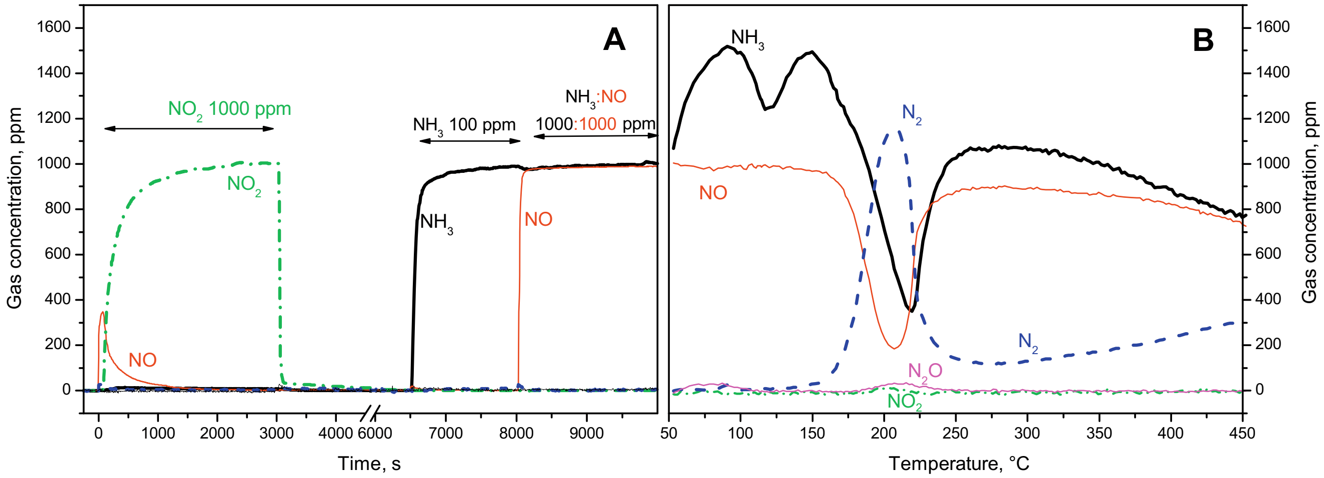

Fig. 2. (A) TRM at 50 °C: NO_2 adsorption (1000 ppm) and nitrates + NH_3 (1000 ppm) + NO (1000 ppm) in a flow of H_2O = 1%, O_2 = 0%, He balance; (B) TPSR: T-ramp at 20 K/min while flowing NH_3 (1000 ppm) + NO (1000 ppm), H_2O = 1%, O_2 = 0%, He balance.

A very similar behavior was reported over a Fe-ZSM-5 catalyst [12]. In both cases, experimental results can be explained considering that, in the presence of ammonia, NO and nitrates, reactions (3)–(6) proceed until depletion of the surface nitrates. This is confirmed by a quantitative analysis of the data: in fact, the molar ratio between NO consumption and N_2 production is close to the 2/3 ratio expected from the combination of reactions (3) and (5), assuming complete conversion of NO_2, as indeed observed. As opposite, the NH_3 consumption/N_2 production ratio evaluated from the data of Fig. 2B is not consistent with that of reactions (3)–(6); however, this is probably due to the ammonia desorption which affects the NH_3 dynamics.

Finally, the deNO$_x$ activity observed above 300 °C could be explained by the Slow SCR reaction (8), coupled with the reduction of residual strongly adsorbed nitrates by NH_3 (9) [13]:

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \tag{8}$$

$$5NH_3 + 3HNO_3 \rightarrow 4N_2 + 9H_2O \tag{9}$$

In fact, the occurrence of the Standard SCR reaction (1) was prevented by the absence of O_2, whereas the quantitative analysis of the curves indicates that the Fast SCR reaction was not occurring, probably because the most part of nitrates was already consumed, and only the strongest adsorbed nitrates were still present. Accordingly, NH_3 and NO could react following the Slow SCR stoichiometry (8), while the nitrates still present could be reduced by NH_3, as discussed in the next paragraph. This is confirmed by the NH_3 consumption and N_2 production, which are higher than those expected from the Slow SCR stoichiometry (8) only.

Experimental data presented in Figs. 1 and 2 provide evidence that nitrates are able to oxidize NO according to reaction (4) already at 50 °C (Fig. 1A); however, in the presence of NH_3 under identical experimental conditions the same reaction does not proceed (Fig. 2A). Accordingly, we can conclude that NH_3 has a blocking effect on reaction (4).

Considering that when NO_2 and ammonia are simultaneously present at low temperature ammonium nitrate forms and deposits onto the catalyst surface, it can be argued that nitrates and ammonium nitrate are characterized by different temperature thresholds in their reactions with NO. Indeed, a higher T-threshold, between 140 and 160 °C, was measured in the presence of ammonia (Fig. 2B): this can be associated with reaction (6), the ammonium nitrate dissociation equilibrium, that at high T is shifted to the left side (i.e. to $NH_3 + HNO_3$), which “frees” nitrates from ammonia, thus allowing the reactions between nitrates and NO (4) to proceed.

Notably, the temperature threshold observed during the TPSR test is quite close to the melting temperature of ammonium nitrate salt (about 170 °C) [15,25]. Accordingly, we propose that in the presence of NH_3 the reaction between NO and nitrates (4) can occur only once equilibrium (6) has been shifted significantly to the left-hand side, either by increasing the temperature [26], or by mass action, i.e. by removing gaseous ammonia.

3.2. NO_2 and NH_3 adsorption tests at low temperature: ammonia–nitrates interaction

To analyze the NH_3–nitrates interaction new TRM tests followed by temperature ramps were performed on the Fe-zeolite catalyst. In this case the TRM tests consists of two subsequent adsorption phases, namely, NO_2 (1000 ppm) and NH_3 (1000 ppm) adsorption at 50 °C, followed by a T-ramp in He to study the desorption/decomposition of surface species.

In the first run (Fig. 3) ammonia is adsorbed first onto a clean catalyst, followed by NO_2 adsorption. In the second run (Fig. 4) the order is reversed: NO_2 is first fed to a clean catalyst, and then NH_3 adsorption is performed.

It appears that during NO_2 adsorption onto a catalyst surface where NH_3 is already adsorbed (Fig. 3A), NO_2 is consumed and NO is produced. Quantitative analysis of the outlet concentration profiles shows that this behavior is in line with nitrates formation by disproportionation of NO_2 (7), just like that observed in the case of a clean catalyst (Fig. 1). Thus such a reaction seems to be essentially unaffected by the presence of adsorbed ammonia on the catalyst surface.

In a previous work [12] we showed that during NO_2 adsorption performed over a Fe-ZSM-5 catalyst at 150 °C in the presence of preadsorbed NH_3, evolution of N_2 instead of NO occurred. The N_2 peak reached 500 ppm and during its evolution NO_2 was totally consumed: the integral amount of produced N_2 corresponded to the amount of NH_3 stored onto the catalyst. A similar result was also found on the present Fe-zeolite catalyst in an identical experiment performed at 200 °C (not reported for brevity). In both cases, N_2 evolution is due to reaction (5): NO_2 disproportionates forming nitrates and nitrites (3) onto the catalyst, and, in the presence of ammonia and at sufficiently high temperatures, nitrites further react with ammonia with formation of ammonium nitrite that decomposes to nitrogen (5) [12].

In the present experiment (Fig. 3A), being the temperature too low, reaction (5) does not take place, and nitrites formed by reaction (3) are further oxidized to nitrates releasing NO according to

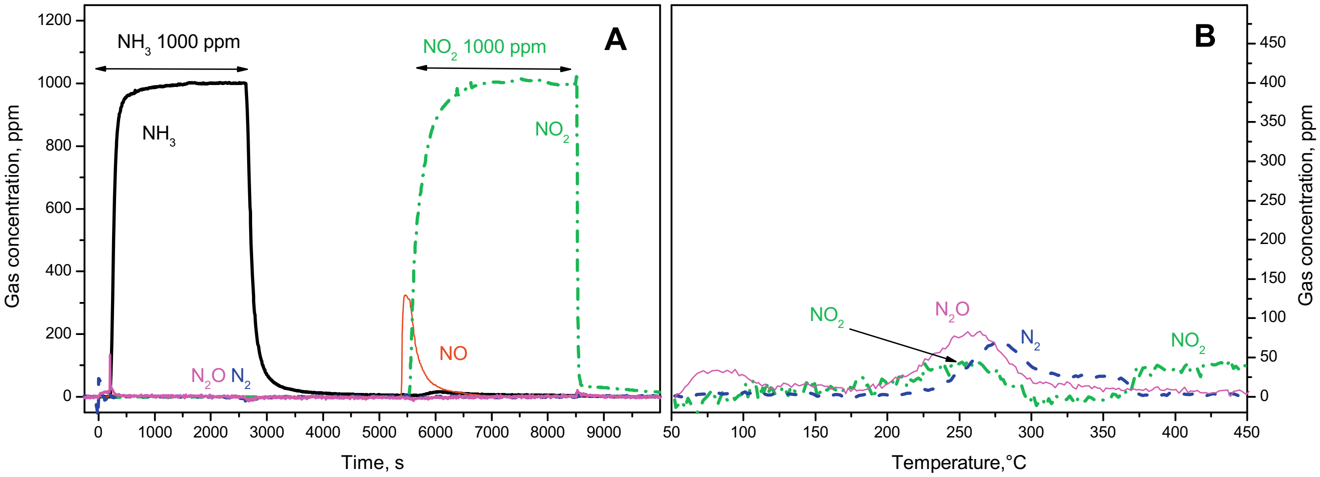

Fig. 3. (A) TRM at 50 °C: NH_3 adsorption (1000 ppm) followed by NO_2 adsorption(1000 ppm) in a flow of $H_2O = 1\%$, $O_2 = 0\%$, He balance; (B) TPD: T-ramp at 20 K/min while flowing He + $H_2O = 1\%$.

reaction (4a = 4 reverse whose addition yields), rather than forming nitrogen via formation/decomposition of ammonium nitrite (5), whose T-threshold is estimated to be around 100 °C.

Fig. 4A shows the results of the second, dual experiment: at 50 °C NO_2 is first fed to the reactor, followed by ammonia. As expected, NO_2 is stored in the form of nitrate species onto a clean catalyst according to the usual overall stoichiometry of reaction (7), and the subsequent ammonia adsorption seems unaffected by the presence of nitrates. Thus the change in the adsorption order between nitrates and ammonia apparently leads to very similar results (Figs. 3A and 4A).

NO_2 and NH_3 storage capacities were evaluated from a quantitative analysis of the TRM tests. In both the runs of Figs. 3 and 4 the amounts of nitrates formed upon NO_2 adsorption were similar (0.0086 and 0.0076 mmol, respectively). As opposite, the NH_3 storage capacity in the absence of preadsorbed NO_2 (Fig. 3) was close to 0.007 mmol, whereas in the second case (Fig. 4), with surface nitrates present, a higher adsorption capacity of 0.012 mmol was measured.

On the other hand inspection of the two subsequent temperature ramps of the TPSR runs (Figs. 3B and 4B) points out significant differences. In the first case (Fig. 3B), we observe evolution of N_2O, N_2, and NO_2 but no NH_3 desorption, while in the second case (Fig. 4B), ammonia evolution is clearly visible in addition.

In both cases, the N_2O peak starts around 200 °C: as discussed in the literature [18,19,27,28], it likely results from ammonium nitrate decomposition:

$$NH_4NO_3 \leftrightarrow N_2O + 2H_2O \tag{10}$$

N_2 evolution starts around 230 °C: it derives from the reduction of nitrates by NH_3 (9):

$$5NH_3 + 3HNO_3 \rightarrow 4N_2 + 9H_2O \tag{9}$$

Such nitrates reduction by NH_3, typical of Lean NO_x Trap catalysis [29,30], has been the object of a separate study over the same Fe-zeolite catalyst [13]: it was shown that gaseous ammonia started reducing nitrates preadsorbed onto the catalyst surface to N_2 at temperatures close to 230 °C.

The absence of ammonia evolution in the first experiment (Fig. 3B), in which NO_2 was fed to the reactor after preadsorbing ammonia, confirms that before the T-ramp only ammonium nitrate was present on the catalyst. This means that nitrates were formed only at catalyst sites where ammonia was present and the process ended up in ammonium nitrate formation. Indeed, in this case NO_2 and ammonia storage capacities were similar.

As opposite, in the second experiment (Fig. 4B), where NH_3 was fed after NO_2, ammonia was adsorbed onto catalyst sites where nitrates were present already, thus forming ammonium nitrate, but

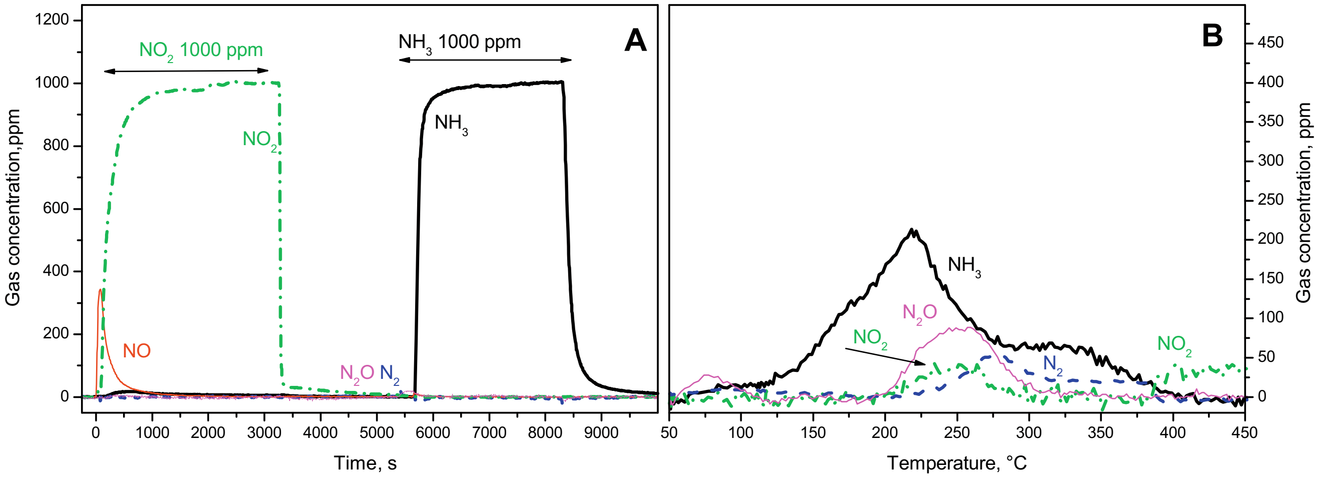

Fig. 4. (A) TRM at 50 °C: NO_2 adsorption (1000 ppm) followed by NH_3 adsorption (1000 ppm) in a flow of $H_2O = 1\%$, $O_2 = 0\%$, He balance; (B) TPD: T-ramp at 20 K/min while flowing He + $H_2O = 1\%$.

also onto other free sites forming simple ammonia adsorbed species. Thus during the T-ramp, N_2O evolution was observed coming from ammonium nitrate decomposition, but desorption of ammonia itself was observed as well. This picture is also confirmed by a quantitative analysis, which showed in this case a significantly higher storage capacity of ammonia with respect to that of NO_2.

Possible interpretations of such data are discussed in the following. NH_3 adsorbs onto the acid sites present on the zeolite surface, while NO_2 should adsorb onto Fe-related sites [13,24,31]. Once surface nitrates are formed, they interact with ammonia, forming ammonium nitrate (or related precursors or strongly interacting ammonia–nitrate species). If ammonia is already present on the catalyst (Fig. 3), once nitrates are formed, ammonia spills onto them and at the end only ammonia–nitrates strongly interacting species are present on the catalyst; during the following T-ramp this results in a typical ammonium nitrate decomposition experiment.

When nitrates are formed first (Fig. 4), on the other hand, gaseous ammonia adsorbs onto them forming the same ammonia–nitrates strongly interacting species, but afterwards ammonia can also adsorb onto other less acidic catalyst sites as well. Thus during the T-ramp, typical ammonium nitrate decomposition products are observed together with ammonia desorption.

In summary, the data in Figs. 3 and 4 clearly evidence a strong interaction between ammonia and nitrates species: we propose that such an interaction can be responsible for the observed ammonia blocking effect on the Fast SCR reactivity.

It is worth emphasizing here that with "blocking" we do not refer to ammonia blocking an active site due to strong chemisorption: rather, NH_3 traps a key intermediate (i.e. surface nitrates) in an unreactive form at low temperatures [14], and releases it again when the temperature is raised.

3.3. NH_3 blocking effect and Fast SCR reactivity

In the previous paragraphs we evidenced a blocking effect played by NH_3 at low temperature on the reaction between NO and nitrate adsorbed species (4), and we attributed such an effect to a strong interaction between surface nitrates and adsorbed ammonia. We proceed now to assess the role of the ammonia blocking effect on the activity of the Fast SCR reaction. For this purpose new transient experiments at 150 and 170 °C are performed and presented in Fig. 5A and B, respectively.

At $t = 0$ s, in a flow of 1000 ppm of ammonia and 1% v/v of water, 500 ppm NO and 500 ppm NO_2 are instantaneously added to the reactor feed stream; then, after signal stabilization, at 8000–8500 s NO_2 and ammonia, but not NO, are removed from the feed flow.

Fig. 5A presents the results of the experiment performed at 150 °C: as NO_x are fed to the reactor, $deNO_x$ activity is observed leading to nitrogen evolution. Such an activity is very high during an initial transient, and then slowly decreases approaching steady state. During the whole reaction phase, NO_2 conversion is higher than that of NO, while NH_3 is consumed in a 1/1 molar ratio with the total NOx. At steady state, NO conversion is negligible, while about 40% of NO_2 and ammonia is still converted to N_2. In addition the atomic N-balance remains below the expected value of 2000 ppm throughout the entire run.

Such a complex behavior is best explained in global terms, considering the simultaneous occurrence of the Fast SCR (2) and of the ammonium nitrate formation reaction (11) [13]

$$2NH_3 + 2NO_2 \rightarrow NH_4NO_3 + N_2 + H_2O \qquad (11)$$

Notice that (11) results from the combination of the crucial steps (3), (5) and (6).

It is important to remark that NO conversion, associated with the Fast SCR activity, is apparent only during the transient part of the run in Fig. 5A, while at steady state only ammonia and NO_2 are consumed producing ammonium nitrate and nitrogen.

At $t = 8000$ s, NH_3 and NO_2 are removed from the feed flow. A sudden drop of their outlet concentrations is first observed, followed by a more gradual decrease, together with NO consumption and N_2 production. The complicated concentration profiles of the different gaseous species are explained by the occurrence of several reactions [13]: ammonium nitrate reduction by NO (12) (i.e. steps (6 reverse) + (4) + (5)),

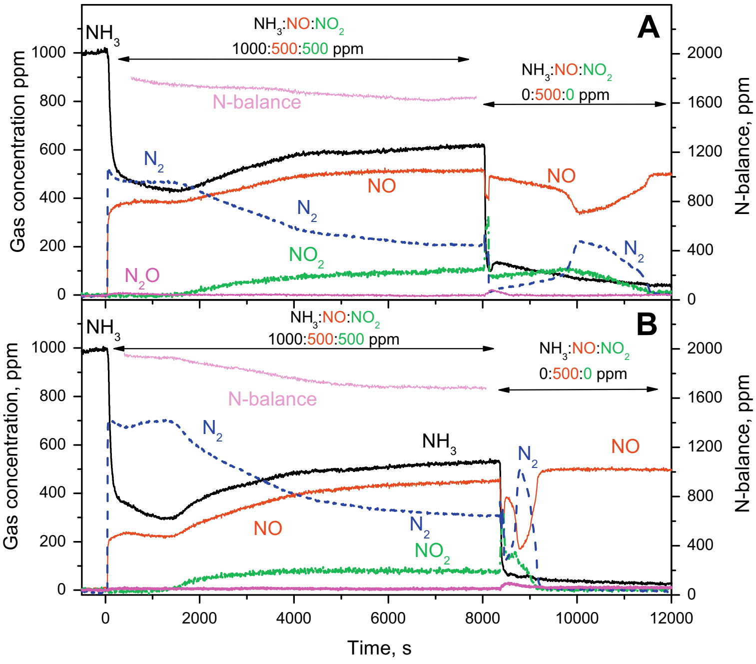

Fig. 5. TRM tests at 150 (A) and 170° (B) NH_3 = 0–1000 ppm, NO = 0–500 ppm, NO_2 = 0–500 ppm, H_2O = 1%, O_2 = 0%, He balance.

$$NH_4NO_3 + NO \rightarrow NO_2 + N_2 + 2H_2O \quad (12)$$

and its partial new formation from NO_2 and ammonia, until its global depletion.

In any case, it is worth noticing that reaction (12), not occurring at steady state in the presence of ammonia–NO/NO_2 mixtures, is restored upon ammonia removal from the feed flow. This is in line with the previously discussed ammonia blocking effect. Indeed, shut off of NH_3 shifts the equilibrium of the ammonium nitrate dissociation reaction (6) to the RHS.

Similar results were obtained at 170 °C (Fig. 5B). At this temperature both the Fast SCR reaction and the ammonium nitrate formation reaction take place in the presence of ammonia, NO, and NO_2. In this case in fact the Fast SCR reaction is more active than at 150 °C, as quantified by the NO consumption at the end of the transient phase (50 ppm at 170 °C vs. 0 ppm at 150 °C).

Also, at $t = 8500$ s when NO_2 and NH_3 are removed from the feed flow, the transients are very similar to those observed at 150 °C, but for a much faster dynamic evolution. Once more in this case the removal of ammonia from the feed flow enhanced the Fast SCR reaction: this can be again associated with the strong interaction between ammonia and nitrates, which tends to block the latter species and prevent their reduction by NO.

It is finally worth mentioning that preliminary results from a parallel investigation on a H-ZSM-5 catalyst have revealed a similar Fast SCR chemistry, though involving formation of a smaller fraction of stable nitrates and characterized by a even stronger inhibition of the crucial reduction of nitrates by NO. In this respect the role of Fe is possibly one of limiting the NH_3–nitrates interaction, thus favoring the active intermediates HNO_3 or nitrates. Such aspects will be systematically investigated in future work.

4. Conclusions

The dedicated transient study performed over the present Fe-Beta catalyst confirmed the reaction mechanism already proposed for the Fast SCR reaction over V-based and Fe-ZSM-5 catalysts, which is based on the key role of the NO reactivity with surface nitrates. New dedicated data showed that such a reaction is already very active at temperatures as low as 50 °C. However, it is virtually stopped by ammonia, whose presence shifts its light-off temperature up to 140–160 °C.

The NH_3 blocking effect is possibly associated with a strong interaction between ammonia and nitrate species when both are present on the catalyst surface. More specifically, at low temperature NH_3 could react with nitrates to form ammonium nitrate precursors (or strongly interacting ammonia–nitrate ad-species), thus blocking the critical reactivity of nitrates with NO.

Since the reduction of nitrates by NO was shown to be the rate determining step of the Fast SCR reaction, the NH_3 blocking effect plays a negative role on the Fast SCR activity as well, introducing an intrinsic limit to the exploitation of this reaction at very low temperatures. In this respect, our data provide direct evidence that the blocking effect of NH_3 on the Fast SCR activity at low temperature occurs not because of the ammonia competitive chemisorption on catalytic sites, but because ammonia captures a key intermediate in an unreactive form.

Experiments showed that one way to partially avoid this undesired effect is to modify the equilibrium of ammonium nitrate dissociation, e.g. by increasing the temperature or by decreasing the gas-phase ammonia concentration. As the blocking effect is strictly related to the acid properties of the formed nitrates, another possibility to moderate its negative impact on the Fast SCR reactivity at low T would be to modify the catalyst acid/base properties in order to favor the interaction between ammonia and the catalyst sites.

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