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NH_3–NO/NO_2 chemistry over V-based catalysts and its role in the mechanism of the *Fast SCR* reaction

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Abstract

We present herein a study performed under transient reactive conditions aimed at elucidating the mechanism of the *Fast SCR* reaction. Transient response data collected at low temperature over a commercial V_2O_5–WO_3/TiO_2 catalyst studying the reactivity of NH_3–NO/NO_2 mixtures with different NO/NO_x feed ratios (from 0 to 1) resulted in the identification of a novel reaction pathway for the *Fast SCR* reaction, which provides a comprehensive description of the chemistry associated with both NH_3–NO_2 and NH_3–NO/NO_2 reacting systems and has been validated step by step by dedicated experiments.

In summary, the first step of the *Fast SCR* reaction is NO_2 dimerization and disproportion to nitric and nitrous acid; then, the presence of adsorbed ammonia species results in the formation of ammonium nitrite, which readily decomposes to N_2 and water, and of ammonium nitrate; this species was found to be a terminal product only in the absence of a suitable reducing agent. When NO is included in the feed, however, it can effectively reduce ammonium nitrate to ammonium nitrite, that once more decomposes to N_2; thus, complete selectivity to N_2 is achieved by adding NO to the NH_3/NO_2 mixture, the optimal expected NO/NO_2 feed ratio being 1/1 as experimentally observed.

Keywords: Diesel–urea SCR; *Fast SCR* reaction; Ammonium nitrate

1. Introduction

It is nowadays worldwide accepted that primary techniques are not sufficient for control of pollutants emitted from vehicles, and thus exhaust after treatment systems are needed in order to comply with the current and the forthcoming emission standards.

Different technologies are being proposed, depending on engines (heavy duty, diesel, gasoline, lean burn ...) and/or on pollutants (NO_x, PM, CO, HY ...); in particular to control NO_x emissions from heavy duty engines, in 2003 the European Association of Car Manufacturers (ACEA) has selected the selective catalytic reduction (SCR) using urea as reducing agent as the most promising solution in view of Euro IV and also Euro V standards [1].

Ammonia SCR is a well-known and widely investigated process, being still after two decades the best commercial technology for efficiency, selectivity and economics in order to control NO_x emissions from stationary sources [2]. The process is based on the *Standard SCR* reaction, whereby one molecule of NO is reduced by one molecule of ammonia in the presence of excess oxygen:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$

Commercial catalysts are honeycomb monolith structures constituted by vanadia and tungsta, the active components, supported on titania: their typical operating temperature window is between 300 and 400 °C.

Extensive work is being currently devoted by the motor industry to adapt the SCR process for deNOxing of stack gases from power stations to the specific demands of mobile applications, as several problems need to be solved, for example, mobile applications rely on the use of urea as a non-toxic reducing agent, which is hydrolyzed on-board to give ammonia; also, there are limitations to the catalyst volume that can be placed on-board; the operating conditions are continuously changing in temperature and flow rate; finally, the

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temperature window has to be enlarged with respect to stationary applications, in particular towards the low-temperature region.

In relation to the last most challenging issue, it has been proposed to use the so called *Fast SCR* reaction [3], in which NH_3 reacts with NO and NO_2 according to

$$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O \quad (2)$$

Reaction (2) is known since the 1980s to be faster by one order of magnitude than the *Standard SCR* at low temperatures [3]. Indeed, it is possible to install on vehicles a pre-oxidizing catalyst upstream from the SCR catalyst that converts part of NO into NO_2.

In this context extensive work has been carried out in our labs, aimed at achieving a quantitative dynamic description of SCR monolithic converters for mobile applications; accordingly, a transient kinetic study of the NH_3–NO/NO_2 reacting system was performed over samples of a single commercial extruded V_2O_5–WO_3/TiO_2 SCR catalyst at different scales, in order to secure the intrinsic kinetics of the different reactions involved (over the catalyst in powder form) and to validate the reactor model and the parameter estimates (over catalysts in monolith form).

In addition, the study of the complete NH_3–NO/NO_2 reacting system has been addressed according to a stepwise approach: the initial analysis was limited to the NH_3/O_2 reacting system, and was then followed by the investigation of the *Standard SCR* reaction (NH_3–NO/O_2 reacting system) [4–6]. At present the study of NH_3–NO/NO_2 complete reacting system and its kinetic analysis is being performed: a preliminary systematic examination of the reactivity of the NH_3–NO/NO_2 SCR system over a wide, representative range of temperatures (175–425 °C) and covering the full range of NO/NO_x feed ratios (from zero to unity) has been recently reported in [7]: the data confirmed that the best DeNO_x efficiency is achieved with a 1/1 NO/NO_2 feed ratio, the main reactions prevailing at the different operating conditions were identified, and an overall reaction scheme suitable for kinetic purposes was proposed.

The analysis of the mechanism of the *Fast SCR* reaction over V_2O_5–WO_3/TiO_2 catalysts was first presented a few years ago by Koebel and co-workers [8–11]: they proposed that the presence of NO_2 in the feed allows a faster reoxidation of the vanadium sites, which is known to be the rate-determining step of the *Standard SCR* reaction below 300 °C. The NO_2-enhanced reoxidation of the catalyst was demonstrated by in-situ Raman experiments [9], but no direct kinetic evidence was provided to confirm that this effect could actually explain the order-of-magnitude increment of the SCR rate.

The mechanism of *Fast SCR* reaction over zeolite-based catalysts has been also addressed by Sachtler and co-workers, mainly by IR techniques [12,13]: the main conclusion of their work was that nitrogen production in the SCR system originates from a fast decomposition of ammonium nitrite, which is unstable above 100 °C; ammonium nitrite would be formed from equimolar NO/NO_2 feeds via formation of N_2O_3 and its reaction with water and ammonia

$$NO + NO_2 \rightarrow N_2O_3 \quad (3)$$

$$N_2O_3 + H_2O + 2NH_3 \rightarrow 2NH_4NO_2 \rightarrow 2N_2 + 4H_2O \quad (4)$$

Indeed the sum of reactions (3) and (4) results in the *Fast SCR* reaction (2).

This reaction scheme, providing a simple, low activation energy pathway for the reduction of nitrogen oxides with ammonia to nitrogen and water, can explain the optimal 1/1 NO/NO_2 feed ratio of the *Fast SCR* reaction on the basis of well-known chemistry. However, the proposed mechanism alone cannot explain all of the several products (N_2, NH_4NO_3, N_2O) observed in SCR reactivity experiments covering the full range of NO/NO_x feed contents [7]. Again, no evidence was provided concerning the compatibility of this pathway with Fast SCR kinetics.

In view of the analysis of the NH_3–NO/NO_2 reacting system, we presented in [14] transient experiments at low temperature over a commercial V_2O_5–WO_3/TiO_2 catalyst, which reveal a novel reaction pathway for the *Fast SCR* reaction. Such data point out a key role of nitrate species and of their reduction by NO in determining the peculiar reactivity and selectivity of the *Fast SCR* reaction: indeed, this reaction would result from the sum of two consecutive steps, namely formation of ammonium nitrate from NO_2 and NH_3 and its reduction by NO [14].

A similar concept has been more recently proposed by Weitz and co-workers [15]: mainly FT-IR data collected over a BaNa–Y zeolite showed that NO can reduce nitric acid, surface nitrates and/or ammonium nitrate, providing different pathways for the production of ammonium nitrite and thus of nitrogen; according to a parallel additional route, however, NO would also react with NO_2 to form N_2O_3 along the lines discussed previously [12,13].

It is apparent that, even if proposals for the mechanism of the *Fast SCR* reaction have been presented in the literature, a comprehensive and detailed reaction scheme able to explain the chemistry and the reactivity of the complete NH_3–NO/NO_2 reacting system covering the full range of NO/NO_x compositions is still lacking.

In this paper new results are shown to complete the picture of the mechanism of the *Fast SCR* reaction in the low-temperature region, and a full proposal for the chemistry that occurs when feeding NH_3–NO_2 and NH_3–NO/NO_2 mixtures over V-based SCR catalysts is presented, discussed and validated on the basis of transient response experiments addressing both the overall reactivity in the *Fast SCR* reaction and also specific individual reaction steps.

2. Experimental

All the SCR runs shown in the present paper were performed over 160 mg of a commercial V_2O_5–WO_3/TiO_2 catalyst, diluted with 80 mg of quartz and loaded in a flow-microreactor consisting of a quartz tube (6 mm i.d.). The catalyst consisted of a powder of 140–200 mesh obtained by grinding an original extruded honeycomb monolith. The reactor was placed into an electric furnace and the reaction temperature was measured and controlled by means of a K-type thermocouple directly immersed in the catalyst bed. NH_3, NO, NO_2, O_2 and He feeds were measured and controlled by mass flow controllers, while water vapour was added by means of a saturator. For specific runs also HNO_3 was fed to the reactor using the same saturator filled with an aqueous solution of nitric acid. The lines were heated up to 200 °C in order to prevent water condensation and deposition of ammonium nitrate. The outlet gas composition was continuously analyzed by means of a quadrupole mass spectrometer (Balzers QMS 200) capable to detect ammonia, NO, NO_2, nitrogen, N_2O, HONO and argon, which was contained in the feed gases and used as an internal standard. The result of the spectrometer analysis was then elaborated considering the cross influences of all species and the response factor (related to the internal standard response factor) of each component previously determined by means of blank experiments. In some experiments ammonium nitrate was collected using a dedicated trap at room temperature located between the reactor and the vent line, thus not interacting with the mass spectrometer. At the end of the experiment the trap was washed with water and the ammonia content of this solution (and hence the nitrate build-up) was determined by Nessler colorimetric analysis.

Helium was used as inert carrier gas in order to allow evaluation of N_2, which is the main SCR product; accordingly, an overall N-balance could be estimated for each run according to the following equation:

$$\text{N-bal} = 100 \times \frac{NH_3^{out} + NO^{out} + NO_2^{out} + 2 \times (N_2^{out} + N_2O^{out})}{NH_3^{in} + NO^{in} + NO_2^{in}}$$

The N-balance always closed within ±5% at steady-state, with the exception of those runs where formation of NH_4NO_3 was significant.

The reactivity of the NH_3–NO/NO_2 SCR system was investigated by transient response methods (TRM experiments), i.e. performing a step change of the inlet concentration of one reactant (NH_3 or NO_x) while feeding the other reactant in the presence of H_2O (1% (v/v)) and balance He at constant temperature. Oxygen (2% (v/v)) was also fed in some experiments, as indicated in the figure captions. The effect of the space velocity was investigated by performing some experiments exactly under the same conditions but varying the gas flow rate between 90 and 120 cm^3/min (STP).

Formation of ammonium nitrate was studied by performing IR characterization of discharged catalyst samples using a ThermoNicolet Nexus Euro Spectrometer.

3. Results and discussion

3.1. NH_3–NO/NO_2 TRM experiments @175 °C

To analyse the reactivity of the NH_3–NO/NO_2 reacting system we performed TRM experiments changing the temperature from 160 up to 425 °C and the feed composition, particularly varying the NO/NO_x feed ratio from 0, i.e. only NO_2 and NH_3, to 1, i.e. only NO and NH_3. The complete set of experiments is reported and discussed elsewhere [7]: in the present work we will focus on the low-temperature region ($T < 200$ °C).

Fig. 1 shows the results collected at 175 °C in the presence of NO_2 in terms of steady-state concentrations of NH_3, NO_x, N_2 and N_2O as a function of the NO to NO_x feed ratio; the nitrogen balance is also plotted.

For NO/NO_x = 0 the feed stream contained only 1000 ppm of NO_2 and 1000 ppm of NH_3, in addition to O_2 and water: in this case analysis of the data reported in the figure shows that we had consumption of 500 ppm of both NH_3 and 500 ppm NO_2 together with the production of 250 ppm of N_2. This stoichiometry suggests the formation of NH_4NO_3 according to

$$2NH_3 + 2NO_2 \rightarrow N_2 + NH_4NO_3 + H_2O \qquad (5)$$

with a conversion of about 50%.

Reaction (5) was already reported in the SCR literature [8,11]: it is known to be favoured at low temperatures in the case of feeds with high NO_2 contents. Unfortunately, NH_4NO_3 cannot be detected by the analysers used in our experiments, but its possible formation is also supported by the lack in the nitrogen balance (solid triangles in Fig. 1): a 25% N-loss can be estimated; with a global feed of 2000 ppm N (1000 ppm of NH_3 + 1000 ppm of NO_2), this amounts to 500 ppm of atomic nitrogen that is exactly in line with the stoichiometry of reaction (5).

From Fig. 1 it also appears that the increment of the NO/NO_x feed ratio, i.e. the addition of NO to the NO_2–NH_3 mixture, was associated with minor changes in both the NO_x and NH_3 conversions, whereas the nitrogen production and simultaneously the nitrogen balance grew significantly with growing NO feed content.

For NO/NO_x equal to 0.5, i.e. for an equimolar NO/NO_2 feed mixture, the N-balance closed to 100% and the selectivity to N_2 was complete, while, as expected, the observed stoichiometry indicated the occurrence of the *Fast SCR* reaction (2).

Thus, according to the data in Fig. 1 the reactivity of the NH_3–NO/NO_2 system at 175 °C is explained by two different

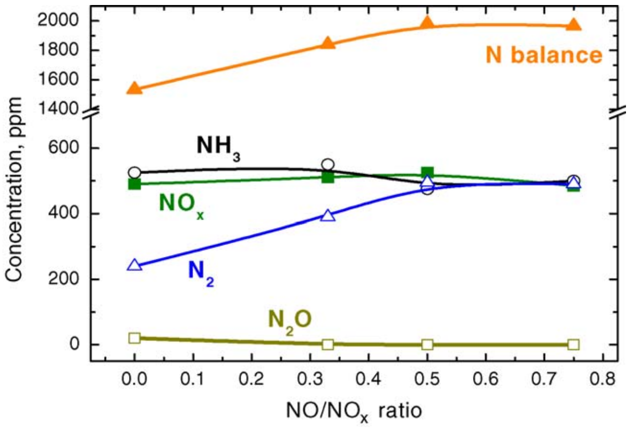


Fig. 1. Steady-state concentrations of NH_3 (open circles), NO_x (solid squares), N_2 (open triangles), N_2O (open squares) and nitrogen balance (solid triangles) vs. NO/NO_x feed ratio for TRM runs at 175 °C: feed, 1000 ppm NH_3; 1000 ppm NO_x; 1% H_2O; 2% O_2 in He; Q = 280 Ncc/min.

reactions, namely the formation of ammonium nitrate (5) and the *Fast SCR* (2): at such a low temperature these two reactions are characterized by a similar reactivity but by a very different selectivity to N_2. To understand if there might be any relations between them, we have then studied the formation of ammonium nitrate in order to establish its occurrence beyond any doubts, and in particular to understand its possible role in the mechanism of the *Fast SCR* reaction.

3.2. NH_4NO_3: formation

To study the reaction of formation of ammonium nitrate two similar experiments at 140 and at 200 °C were performed by cofeeding NO_2 and NH_3 (Fig. 2) in a continuous flow of O_2 (2%) and H_2O (1%) + He. In the former run, 1000 ppm of NH_3 were admitted to the reactor at $t = 0$ s while feeding 1000 ppm of NO_2 in He; in the experiment performed at 200 °C at $t = 0$ s 1000 ppm of NO_2 were added to a feed stream constituted by 1000 ppm NH_3 in He: in both cases we observed an immediate consumption of both reactants and a simultaneous production of nitrogen, and at the same time the nitrogen balance was below 100%. The steady-state values of NO_2, NH_3 and N_2 and the lack in the N-balance confirmed the occurrence of the reaction of formation of ammonium nitrate (5), for which a conversion of roughly 60% was measured at 140 °C, while at 200 °C the conversion increased up to 70%.

To verify if ammonium nitrate was actually formed and deposited onto the catalyst during those experiments, at the end of the runs the two catalyst samples were downloaded and analysed by IR.

Fig. 3 shows the IR spectra of pure ammonium nitrate, of the fresh catalyst and of the two different batches of catalyst discharged after the occurrence of reaction (5) between ammonia and NO_2 at 140 and 200 °C.

The spectrum of pure NH_4NO_3 shows bands at 1380 and at 3150 cm^{-1}; the fresh catalyst is characterized by two peaks at 1070 and 1630 cm^{-1} and a large band at about 3400 cm^{-1}. The catalyst downloaded after the TRM run performed feeding NH_3 and NO_2 at 140 °C exhibited all the IR bands of both the fresh catalyst and the ammonium nitrate, thus proving that under these conditions the formed NH_4NO_3 is indeed deposited onto the catalyst. On the other hand the IR spectrum performed upon a second batch of the same catalyst downloaded after the similar experiment at 200 °C showed no differences with the spectrum of the fresh catalyst. This result suggests that, if the reaction between NH_3 and NO_2 is carried out at 200 °C, ammonium nitrate is formed, because reaction (5) still occurs as demonstrated in Fig. 2, but is not deposited upon the catalyst.

The above observations are in agreement with the thermodynamic properties of NH_4NO_3, which is known to be solid below about 170 °C and to sublimate or decompose at higher temperatures according to the following equilibrium [16,11]

$$NH_4NO_3 \Leftrightarrow NH_3 + HNO_3 \qquad (6)$$

Accordingly, when ammonium nitrate is formed below such a threshold temperature, it builds up onto the catalyst surface.

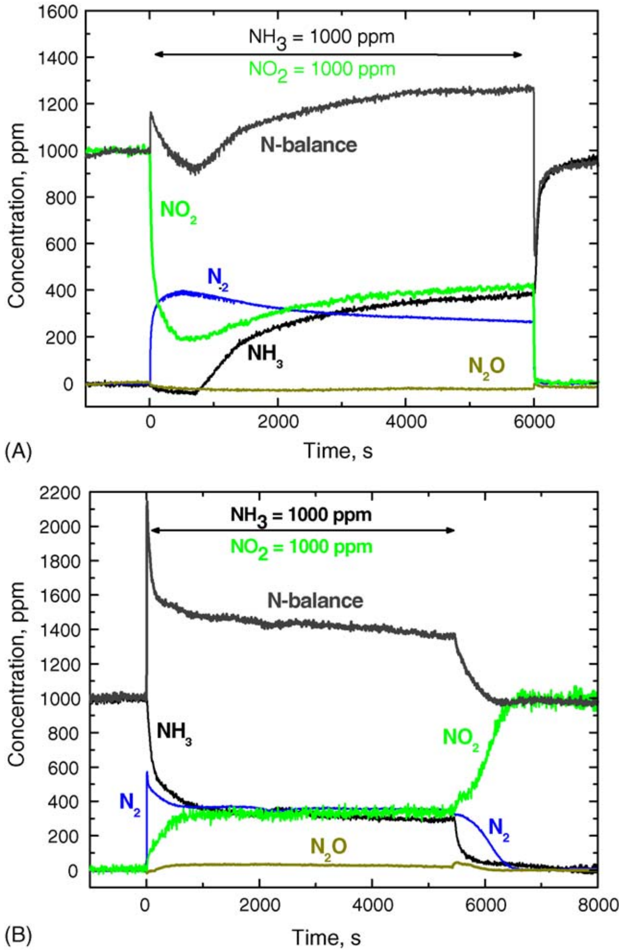


Fig. 2. Transient experiments: formation of NH_4NO_3. Feed, 1000 ppm NH_3; 1000 ppm NO_2; 1% H_2O; 2% O_2 in He; Q = 120 Ncc/min; (A) T = 140 °C and (B) T = 200 °C.

On the other hand, if its formation occurs at $T > 170$ °C it is immediately decomposed into its gaseous decomposition products $NH_3 + HNO_3$, which flow downstream from the reactor; however, as soon as such species reach a cold spot along the lines (for example just before the entrance orifice of the mass spectrometer, which operates at 80 °C for instrumental reasons), the equilibrium is shifted back towards the solid nitrate. This explanation is consistent with the observation of white solid ammonium nitrate deposited in cold parts of the rig, and also explains why the N-balance loss discussed above does not disappear when the experiment is performed at $T > 170$ °C: in fact, even if the nitrate is not stored upon the catalyst, it is in any case deposited upstream from the analysis device.

To attain a final quantitative proof of this behavior, the cold trap described in Section 2 was included in the rig downstream from the reactor, in order to collect the ammonium nitrate or its decomposition products in the reactor effluents. The NO_2/NH_3 TRM run at 200 °C shown in Fig. 2 was replicated: at the end of the experiment the trap was washed with water and the resulting solution analysed for its N-content. The amount of ‘‘trapped’’ ammonium nitrate resulted in good agreement with the amount expected according to (5) from the steady-state values

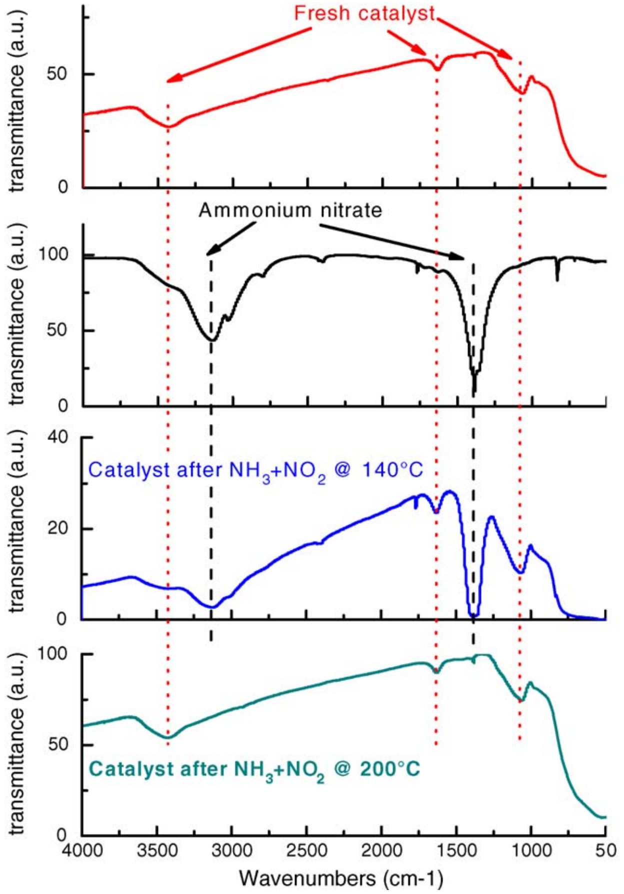


Fig. 3. Comparison of IR spectra of fresh V_2O_5–WO_3/TiO_2 catalyst, commercial NH_4NO_3 and catalyst discharged after reaction of NH_3 and NO_2 at 140 and 200 °C.

measured during the experiment [7]. Accordingly, the cold trap, coupled with the mass-spec, allowed quantification of all of the species involved in the reaction network, thus overcoming the balance loss observed in Fig. 1 at lower temperatures: to our knowledge, closure of the N-balance had not been reported before for NO_2/NH_3 reactivity experiments under these conditions.

The role of the catalyst in the formation of ammonium nitrate was also addressed. To clarify this aspect, we run similar experiments feeding NO_2 and NH_3 in O_2 (2%), H_2O (1%) and He either in the presence or in the absence of the V-based catalyst: in the latter case only inert particles were loaded in the reactor. Results are reported in Fig. 4 in terms of outlet concentrations of NH_3, NO_2, N_2 and N_2O. As opposite to the case, already discussed, of the TRM performed at 200 °C in the presence of the catalyst (see Fig. 2), NH_3 and NO_2 did not react when no catalyst was present in the reactor; even after lowering the temperature down to 100 °C no reaction was observed. This result indicates that at temperatures higher than 100 °C the formation of NH_4NO_3 is not a homogeneous reaction occurring in the gas phase.

Once verified and quantified the formation of ammonium nitrate, the analysis of the entire set of data collected performing experiments feeding NO_2 and NH_3 only over a V_2O_5–WO_3/TiO_2 SCR catalyst in the low temperature region, coupled with the analysis of literature information, can be used to clarify and identify the detailed chemistry of this reacting system, as depicted in Scheme 1 (dashed box).

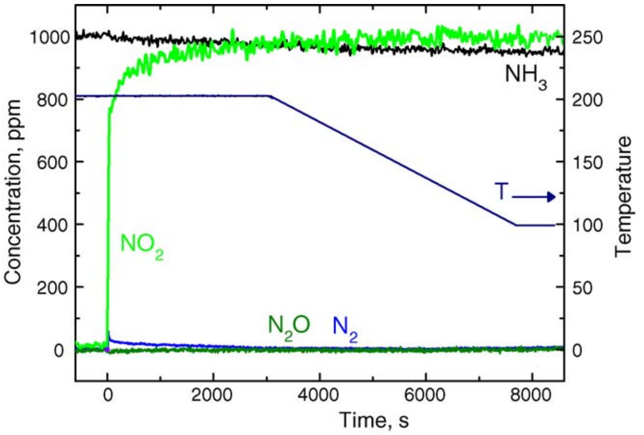


Fig. 4. TRM run performed with no catalyst at 200 °C followed by decreasing T ramp down to 100 °C: feed, 1000 ppm NH_3; 1000 ppm NO_2; 1% H_2O; 2% O_2 in He; Q = 280 Ncc/min.

We believe that the first step of the observed reactivity between NO_2 and NH_3 is NO_2 disproportion to nitrous and nitric acid via NO_2 dimerization and reaction with water:

$$2NO_2 \leftrightarrow N_2O_4 \tag{7}$$

$$N_2O_4 + H_2O \leftrightarrow HONO + HNO_3 \tag{8}$$

This chemistry is indeed well-known from nitric acid plants [16].

In the presence of NH_3 species adsorbed onto the catalyst, however, nitrous acid forms ammonium nitrite which, as already known from the middle of the 19th century [12,13,17], then readily decomposes to N_2:

$$HONO + NH_3 \rightarrow [NH_4NO_2] \rightarrow N_2 + 2H_2O \tag{9}$$

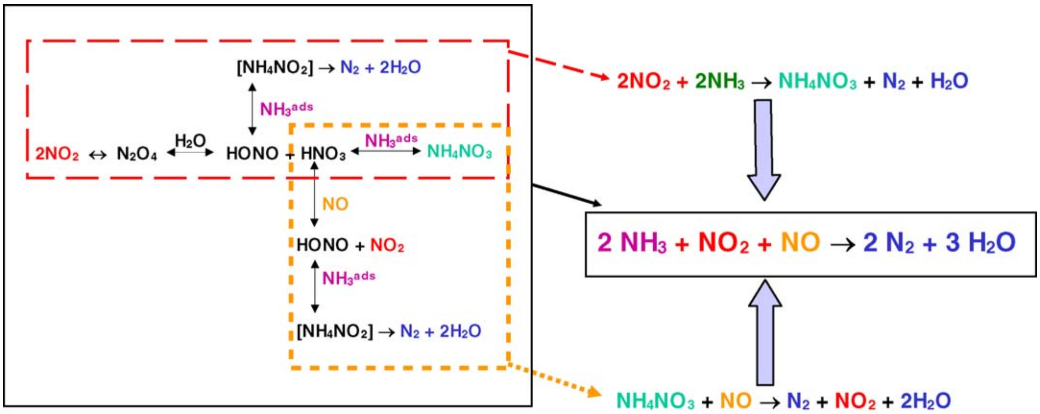
Of course, also nitric acid reacts with adsorbed NH_3 to form ammonium nitrate, which at low temperature eventually builds up onto the catalyst.

Accordingly, when feeding NO_2 and NH_3 the overall observed reaction is the formation of ammonium nitrate and of N_2, reaction (5). It is worth emphasizing that during our experiments this kind of reactivity was quite effective already at temperatures as low as 140 °C.

3.3. *NH_4NO_3: reaction with NO*

In the previous paragraph data have been presented showing that the reactivity of NO_2/NH_3 mixtures, so without NO, in the low temperature region leads to formation of ammonium nitrate and its build up onto the catalyst. However, it is clear from Fig. 1 that, to reach a 100% selectivity to N_2, NO must be added to the reacting system in order to achieve the 1/1 NO/NO_2 molar ratio associated with the occurrence of the *Fast SCR* reaction.

To understand the relation between such two reaction regimes, and to clarify the possible role of nitrates in the *Fast*



Scheme 1. Chemistry of NH_3/NO_2 (dashed box) and of NH_3–NO/NO_2 (solid box) SCR reacting systems over V_2O_5–WO_3/TiO_2 SCR catalysts.

SCR reaction, in a second step of our investigation we have then addressed the reactivity of ammonium nitrate with NO.

Fig. 5A and B shows the results of two similar experiments performed at 170 °C with different space velocities. The runs can be separated in three different and subsequent stages: in the first one NH_3 and NO_2 were fed to the reactor in order to form and deposit ammonium nitrate onto the catalyst; during the second part NO_2 was removed from the feed stream while ammonia was still being fed to preserve the deposited NH_4NO_3 from decomposition to NH_3 and nitric acid according to (6); in the third part of the experiment NO was admitted to the reactor where residual ammonium nitrate was present.

Concerning the first part of both experiments in Fig. 5, the results were in line with the data shown above (Fig. 2) concerning the formation of ammonium nitrate; indeed, addition of ammonia to an NO_2 feed stream resulted in consumption of both reactants and in the production of nitrogen and of ammonium nitrate, as monitored by the lack in the nitrogen balance. In both cases, the steady-state levels of NO_2, NH_3 and N_2 as well as the lack in the N-balance confirmed the occurrence of reaction (5).

When at the end of the first part NO_2 was removed from the feed, only NH_3 was fed over the catalyst where ammonium nitrate was present: the data in Fig. 5 show that NH_3 was not able to react with this species, and indeed its outlet concentration reached rapidly the feed concentration value.

On the contrary, quite a different behaviour was apparent during the third final stage of the experiment, when NO was added to the reacting system. In this case Fig. 5 points out an equimolar consumption of NO and NH_3 accompanied by the production of N_2: this reaction, however, goes through a transient and eventually stops, indicating that NH_4NO_3, still present on the catalyst at the end of the second part of the run was also being consumed. Until its depletion, however, the reaction proceeded in line with the following stoichiometry

$$(1/2)NH_4NO_3 + NO + NH_3 \rightarrow (3/2)N_2 + (5/2)H_2O \qquad (10)$$

As already discussed in [14], such an observed stoichiometry results from the occurrence of two consecutive reactions. The former one involves the reduction of the deposited ammonium nitrate by NO, which is concurrently oxidized to NO_2; in a second step, such NO_2 can further react with excess NH_3 to form more NH_4NO_3 and N_2 according to reaction (5), as discussed in the previous section.

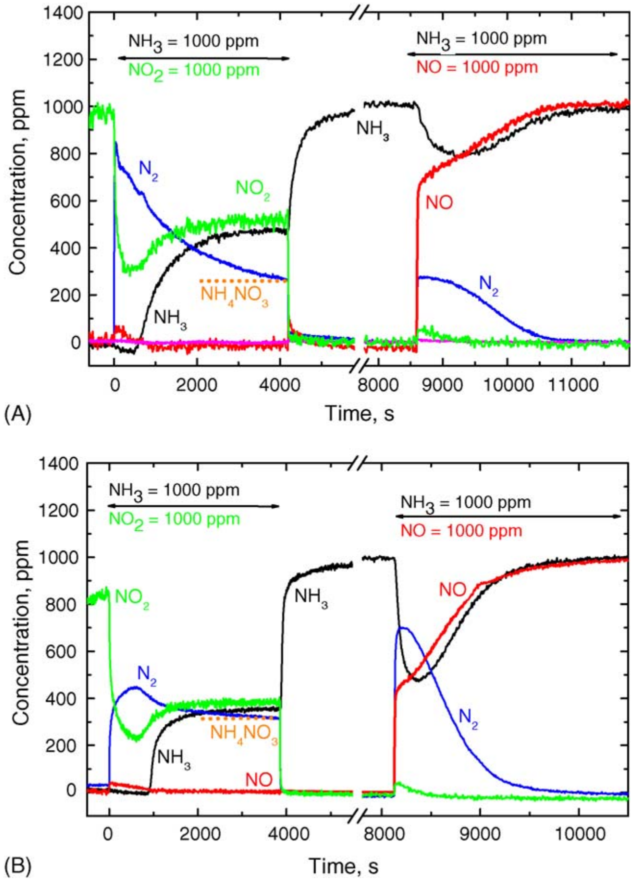


Fig. 5. Transient experiment at T = 170 °C: formation of NH_4NO_3 (feed, 1000 ppm NH_3; 1000 ppm NO_2; 1% H_2O in He); reduction of NH_4NO_3 by NO (feed, 1000 ppm NH_3; 1000 ppm NO; 1% H_2O in He); (A) Q = 120 Ncc/min and (B) Q = 90 Ncc/min.

Thus, one could e.g. write reaction (10) formally as the sum of [14]

$$2NH_4NO_3 + NO \rightarrow 3NO_2 + 2NH_3 + H_2O \qquad (11)$$

$$3NO_2 + 3NH_3 \rightarrow (3/2)NH_4NO_3 + (3/2)N_2 + (3/2)H_2O \qquad (5)$$

where the global reaction (11), resulting from dissociation of NH_4NO_3 according to (6) followed by reduction of HNO_3 by NO, was invoked by Koebel et al. [11] to describe the reaction between NH_4NO_3 and NO observed at 150 °C over V-based SCR catalysts. We prefer, however, to adopt the following alternative stoichiometry, which is possibly closer to the real chemical mechanism:

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

$$NO_2 + NH_3 \rightarrow (1/2)NH_4NO_3 + (1/2)N_2 + (1/2)H_2O \qquad (5)$$

The overall reaction (12) implies, in fact, that NO reduces NH_4NO_3 to ammonium nitrite, which then decomposes to N_2 and water. Notice that both the sum of (11) and (5), and the sum of (12) and (5), yield the observed reaction (10).

Irrespective of the reaction sequence adopted for their rationalization, it clearly appears from the results in Fig. 5 that, in the presence of NO, NH_4NO_3 behaves no longer as a terminal product: already at low temperatures NH_4NO_3 does actively react with NO, being reduced by it and forming NO_2. In the presence of NH_3, the net result of this process is its eventual complete conversion to N_2.

3.4. NH_4NO_3: role in the *Fast SCR* reaction

In the previous sections we have shown that the reactivity of the NH_3–NO/NO_2 system at low temperature is associated with two different reactions, namely the formation of ammonium nitrate (5) and the *Fast SCR* reaction (2), which exhibit similar reactivities but very different selectivities to N_2. Furthermore, we have confirmed that ammonium nitrate is reactive under the same conditions, too, being reduced by NO with production of nitrogen according to (10).

In fact the occurrence of all the three reactions (2), (5) and (10) for NH_3–NO/NO_2 SCR over V-based catalysts had been reported previously [8–11]. So far, however, formation of ammonium nitrate, reaction (5), and its reduction, reaction (10), have been regarded as independent side reactions which occur in parallel to the *Fast SCR* reaction (2). In the light of the results herein presented, such an assumption seems nonetheless at variance with the similar NO_x conversions afforded by reactions (2) and (5) at the conditions of Fig. 1.

Accordingly, in this section we proceed to explore possible closer relationships among reactions (2), (5) and (10). In order to address this point, two additional transient reactive experiments were performed at 170 °C at different space velocities, with results shown in Fig. 6A and B. In this case, at $t = 0$ s both NO and NO_2 (500 and 500 ppm) were admitted to the reactor while feeding 1000 ppm of ammonia in He: under these conditions, the simultaneous occurrence of the *Fast SCR* reaction (2) and of formation and deposition of ammonium nitrate, reaction (5), were observed at both space velocities.

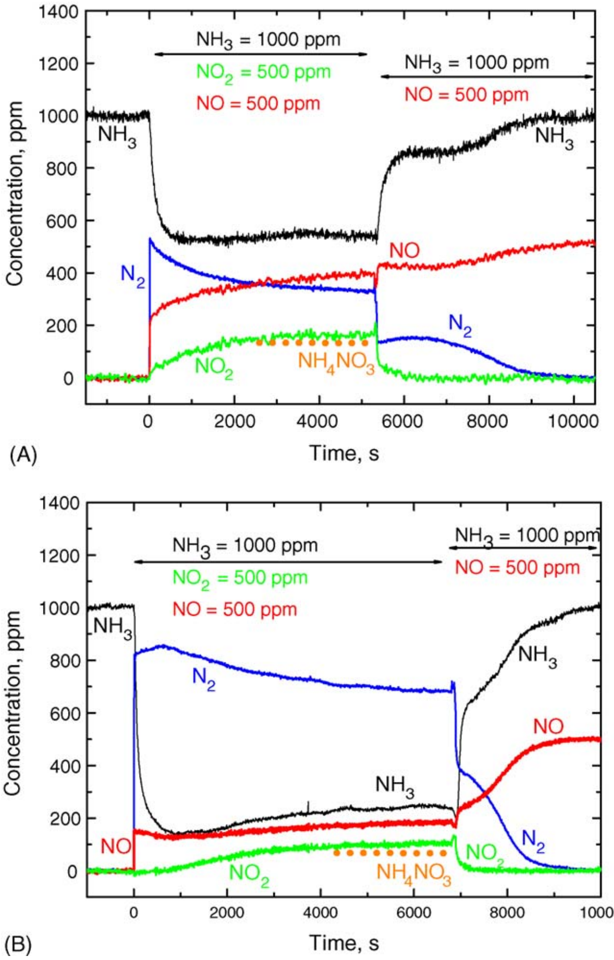


Fig. 6. Transient experiment at $T = 170$ °C: *Fast SCR* reaction and formation of NH_4NO_3 (feed, 1000 ppm NH_3; 500 ppm NO_2; 500 ppm NO; 1% H_2O in He); reduction of NH_4NO_3 by NO (feed, 1000 ppm NH_3; 500 ppm NO; 1% H_2O in He); (A) $Q = 120$ Ncc/min and (B) $Q = 90$ Ncc/min.

The extent of the *Fast SCR* reaction is indicated by the conversion of NO, which is involved as reactant only in this reaction: the NO conversion was roughly 10% in the experiment with the higher space velocity (Fig. 6A) and 30% in the second one (Fig. 6B); on the other hand, NH_3 and NO_2 were consumed to a greater extent because they reacted also according to (5), as expected. For example, in the first run, 200 ppm of ammonia reacted with 100 ppm of NO and 100 ppm of NO_2, producing 200 ppm of N_2 via the *Fast SCR*, but additional 300 ppm of ammonia and 300 ppm of NO_2 reacted forming 150 ppm of nitrogen and 150 ppm of ammonium nitrate, which was deposited onto the catalyst.

When the concentration profiles reached steady state, NO_2 was then removed from the feed stream, whereas NO and ammonia were still being fed onto the catalyst where ammonium nitrate was present. This is the situation where reaction (10) takes place, and indeed the consumption of NO and NH_3 as well as the simultaneous production of nitrogen observed in both Fig. 6A and B agree with the stoichiometry of reaction (10).

But the data in Fig. 6 also show that the NO concentration level before NO_2 removal, which is determined by the occurrence of the *Fast SCR* reaction, and the NO concentration level after NO_2 removal, which is determined by the reaction between ammonium nitrate and NO, remained more or less identical.

This important result points out that the rate of the reaction between NH_4NO_3 and NO was essentially equal to that of the *Fast SCR* reaction, which rules out the assumption that the two reactions proceed in parallel. Accordingly, we propose instead a sequential scheme, whereby the *Fast SCR* reaction (2) results from the formation of NH_4NO_3, reaction (3), and its subsequent reduction by NO, reaction (12):

$$2NH_3 + 2NO_2 \rightarrow N_2 + NH_4NO_3 + H_2O \qquad (3)$$

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

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \qquad (2)$$

It is worth emphasizing that this reaction scheme is able to explain not only the stoichiometry of the *Fast SCR* reaction, and specifically the optimal equimolar NO to NO_2 feed ratio, but as well the selectivity to all of the observed products, namely N_2, NH_4NO_3 and N_2O (which derives from thermal decomposition of ammonium nitrate [10,16]), and is also in agreement with the observed kinetics of the *Fast SCR* reactions, which at low temperature is limited by the reaction between NH_4NO_3 and NO.

The collected data allow extending the picture of the SCR chemistry in Scheme 1 to the analysis of the full NO–NO_2/NH_3 system (solid box). Even in the presence of NO, the chemistry of the NO_2/NH_3 reacting system described in previous sections is still proceeding over the catalyst (dashed box): through dimerization, disproportion and reaction with water NO_2 is converted to nitrous and nitric acid (reactions (7) and (8)), which, in the presence of adsorbed ammonia, form, respectively, NH_4NO_2, from which nitrogen is readily produced (reaction (9)), and NH_4NO_3 (reaction (6) reverse), which in the absence of a suitable reducing agent behaves as a terminal product, or may be thermally decomposed to N_2O at higher temperatures.

But the introduction of NO into the reacting system allows the reduction of ammonium nitrate (dotted box). Actually, we have shown that NH_4NO_3 is in equilibrium with ammonia and nitric acid; it is likely that HNO_3 oxidizes NO to NO_2, being reduced to nitrous acid:

$$HNO_3 + NO \Leftrightarrow HONO + NO_2 \qquad (13)$$

Then, as already observed, in the presence of adsorbed NH_3 nitrous acid produces N_2, via decomposition of NH_4NO_2 (reaction (9)).

As depicted in the lower part of Scheme 1, the sum of the individual reactions starting from ammonium nitrate and NO results in the global reaction (12), that was confirmed experimentally [8].

If we now couple the observed overall reaction summarizing the chemistry of the NO_2/NH_3 system (reaction (5)) with that describing the addition of NO to this reacting system (reaction (12)), we recover the well-known stoichiometry of the *Fast SCR* reaction (2).

A similar chemistry has been very recently proposed by Weitz and co-workers [15]. Working on BaNa–Y zeolite in the presence of NO_2/NH_3 these authors have shown that NO_2 plays a critical role, being involved in a number of different parallel reactions eventually leading to ammonium nitrite, which decomposes to nitrogen. Starting from NO_2, in fact, dimerization occurs as the first step, from which nitric acid, surface nitrates and ammonium nitrate can be possibly formed; NO was found able to reduce all of those species to nitrites. In addition, nitrites could also be directly formed via gas phase reaction between NO and NO_2. From this paper it appears that different reactions can occur when feeding NH_3–NO/NO_2 mixtures: while they all seem in line with the results herein presented, the data in [15] did not allow to discriminate among several possible parallel routes.

3.5. Reactivity of nitric acid

To confirm the NH_3–NO/NO_2 SCR chemistry proposed in Scheme 1, and specifically to verify the role of nitric acid as the reactive intermediate, we have also investigated directly the reactivity of this species with NO.

Fig. 7 shows the results of a dedicated transient experiment at 200 °C: while feeding about 50 ppm of nitric acid (not detectable by the mass-spec) in He carrier gas, 1000 ppm of NO were instantaneously admitted to the reactor at $t = 0$ s. It clearly appears from the figure that the added NO reacted with all the nitric acid, and a production of both NO_2 ($\sim$50 ppm) and nitrous acid (not quantified) was detected, in line with reaction (13).

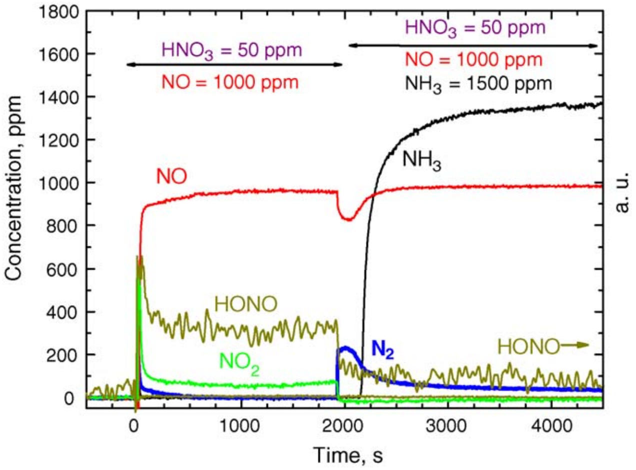


Fig. 7. Transient experiment at $T = 200$ °C: reactivity of HNO_3 with NO (feed, 1000 ppm NO; 50 ppm HNO_3; 1% H_2O in He); reactivity of HNO_3 with NO and NH_3 (feed, 1500 ppm NH_3; 1000 ppm NO; 50 ppm HNO_3; 1% H_2O in He); $Q = 120$ Ncc/min.

In a second stage of the experiment, at $t = 1900$ s 1500 ppm of ammonia were also added to the reactor feed: the NH_3 outlet concentration remained at 0 ppm for some minutes, indicating its complete consumption due to adsorption onto the catalyst and reaction; consumption of NO_2, HONO and NO, and simultaneous production of nitrogen were also observed. This behaviour is explained considering that the introduction of ammonia into the reactor allowed the occurrence of reaction (9) between nitrous acid and ammonia, forming nitrogen via decomposition of NH_4NO_2. Furthermore, NO_2 formed from (13) could now react with ammonia according to reaction (5) to yield more nitrogen and ammonium nitrate: this species was also in equilibrium with ammonia and nitric acid (reaction (6)), and could thus react further in the presence of NO.

In summary the data in Fig. 7 confirm the whole set of reactions involving HNO_3, NO and NH_3 depicted in Scheme 1, which end up with the production of nitrogen. Considering the different consecutive steps observed during the experiment, in fact,

$$HNO_3 + NO \Leftrightarrow NO_2 + HONO \tag{13}$$

$$HONO + NH_3 \rightarrow [NH_4NO_2] \rightarrow N_2 + 2H_2O \tag{9}$$

$$NH_3 + NO_2 \rightarrow (1/2)N_2 + (1/2)NH_4NO_3 + (1/2)H_2O \tag{5}$$

$$(1/2)NH_4NO_3 \Leftrightarrow (1/2)NH_3 + (1/2)HNO_3 \tag{6}$$

$$(1/2)HNO_3 + NO + (3/2)NH_3 \rightarrow (3/2)N_2 + (5/2)H_2O \tag{14}$$

we obtain an overall stoichiometry which is roughly respected in the experiment, considering the analytical uncertainties.

The present results also confirm that nitric acid can be the intermediate in reaction (12) between ammonium nitrate and NO, and can also explain the small increase in the NO concentration observed in Fig. 6 when NO_2 was removed from the feed stream: indeed, the simultaneous increase in the NH_3 concentration shifted equilibrium (6) to the left, thus decreasing the concentration of HNO_3 that was reacting with NO.

4. Conclusions

SCR using urea as reducing agent is regarded as the technology of choice for the abatement of NO_x from the exhausts of heavy-duty diesel vehicles to comply with the next European regulations. In particular, the *Fast SCR* reaction for which NH_3 reacts with NO and NO_2 is currently widely investigated, as it can extend the operating window in the low temperature region.

We have herein presented a dedicated study over a commercial V_2O_5–WO_3/TiO_2 catalyst under transient conditions, aimed at the elucidation of the mechanism of the *Fast SCR* reaction.

Transient data collected at low temperature studying the reactivity of NH_3–NO/NO_2 mixtures with different NO/NO_x ratio (from 0 to 1) have allowed identification of a novel reaction pathway for the *Fast SCR* reaction; a comprehensive description of the chemistry that occurs when feeding NH_3/NO_2 and NH_3–NO/NO_2 mixtures has been presented, discussed and validated step by step by dedicated experiments.

Concerning the reactivity between NO_2 and NH_3, it is proposed that NO_2 via dimerization, disproportion and reaction with water leads to nitrous and nitric acid, which, in the presence of ammonia adsorbed species, form, respectively, NH_4NO_2, from which nitrogen is readily produced, and NH_4NO_3; in the absence of a suitable reducing agent ammonium nitrate behaves as a terminal product, or may be thermally decomposed to N_2O at higher temperatures.

But the introduction of NO into the reacting system allows reduction of ammonium nitrate through reaction between nitric acid (in equilibrium with ammonium nitrate) and NO; as a matter of facts, dedicated experiments herein presented confirm that nitric acid is able to oxidize gaseous NO to NO_2, being reduced to nitrous acid. Then in the presence of adsorbed NH_3 nitrous acid produces N_2, via decomposition of NH_4NO_2.

The well-known stoichiometry of the *Fast SCR* reaction, Eq. (2), is readily recovered once we couple the observed overall reaction summarizing the chemistry of the NO_2/NH_3 system with that describing the addition of NO to this reacting system.

So in the full NH_3–NO/NO_2 reacting system (*Fast SCR*), the selectivity to N_2 is ruled by the formation of NH_4NO_2 that decomposes to N_2, but also by the formation of NH_4NO_3 that is reduced to NH_4NO_2 by NO. Accordingly, NO_2 is responsible for the formation of nitrites and nitrates, the key role of NO is to reduce nitrates to nitrites, and eventually ammonia allows formation of ammonium nitrite, which is the direct precursor of the desired nitrogen product.

The proposed reaction scheme was found able to describe not only the stoichiometry of the *Fast SCR* reaction, and specifically the optimal equimolar NO to NO_2 feed ratio, but also the selectivity to all of the observed products, namely N_2, NH_4NO_3, HNO_3 and N_2O; furthermore, it is in agreement with the observed kinetics of the *Fast SCR* reaction, which at low temperature is limited by the reaction between HNO_3 and NO.

Such reaction pathways provide the basis for the development of a chemically consistent kinetic model of the Fast SCR system.

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