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A study of the mechanism of selective conversion of ammonia to nitrogen on Ni/γ-Al_2O_3 under strongly oxidising conditions

M. Amblard[1], R. Burch[*,2], B.W.L. Southward[2]

Catalysis Research Centre, Department of Chemistry, The University of Reading, Whiteknights, Reading RG6 6AD, UK

Abstract

The activity and excellent selectivity (>90%) of γ-Al_2O_3-supported Ni for the selective catalytic oxidation (SCO) of NH_3 to N_2 with excess O_2 has been shown by microreactor studies. Further studies of the mechanism involved in this reaction have been carried out using TPD, TPO, TPReaction as well as DRIFTS. N_2H_4 and NO have been used to model the intermediates of the SCO mechanism (direct formation of N_2 via the recombination of two NH_x species) and of the in situ SCR mechanism (two-step formation of N_2 via the reduction of an in situ produced NO species by a NH_x species), respectively. Two IR absorption bands appear during the TPO of NH_3 in the temperature range of N_2 formation and have been assigned to stable bidentate nitrate surface species. This represents strong evidence that under the present conditions, formation of N_2 occurs via the in situ SCR mechanism. This also explains the sudden "NO jump" observed on various systems once the temperature is high enough to activate $\sim 50\%$ of the NH_3 molecules fed to the catalyst. The fact that NO and NH_3 are able to react to give N_2 at low temperature (from 100°C) confirms that activation of NH_3 is the limiting step. In contrast, no evidence has been found to support the possibility of the SCO mechanism.

Keywords: Selective ammonia oxidation; In situ SCR; Nitrogen; Nitrate; Nickel; DRIFTS

1. Introduction

Increasing pressures are being imposed on industry and agriculture to adopt environmentally cleaner processes. Ammonia (NH_3) abatement is a particular challenge to be addressed. It is known to be a primary pollutant causing severe irritation and burns and is suspected to have long-term effects such as bronchitis. The major source of NH_3 emission has been attributed to the intensive farming areas and notably to livestock manure. This has led to a recent study of the role of NH_3 in the formation of a rural version of urban smog [1].

In contrast, NH_3 is used beneficially in industry to reduce NO_x emissions by the so-called selective catalytic reduction process (SCR). It is added to the effluent as reductant in order to perform the following reaction:

$$NH_3 + NO + \tfrac{1}{4}O_2 \rightarrow N_2 + \tfrac{3}{2}H_2O \qquad (1)$$

However, the reaction is complete only with an excess of NH_3, giving rise to NH_3 "slip".

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[*] Corresponding author. Present address: The School of Chemistry, The Queen's University of Belfast, David Keir Building, Stranmillis Road, Belfast BT9 5AG, Northern Ireland, UK. Tel.: +44-1232-245133; fax: +44-1232-382117.
E-mail address: r.burch@qub.ac.uk (R. Burch)

[1] Present address: Laboratoire de Physico-Chimie des Interfaces et Applications, Université d'Artois, Faculté Jean Perrin, rue Jean Souvraz, SP 18, 62307 Lens Cedex, France.

[2] Present address: The School of Chemistry, The Queen's University of Belfast, David Keir Building, Stranmillis Road, Belfast BT9 5AG, Northern Ireland, UK.

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NH_3 is also a potential source of nitrogen oxides (NO_x) when involved in conventional combustion [2]. A typical example is the production of energy by combustion of gasified biomass. Several projects addressing combined heat and power generation using turbines and heat-recycling systems are ongoing [3–4]. The use of biomass as a primary fuel is particularly interesting since it offers the possibility of no net emission of CO_2. It is also flexible for use in small units for remote locations where no other fuel is available. However, biomass contains significant quantities of fuel-bound nitrogen. Gasification results in the formation of NH_3 (600–4000 ppm) in addition to CO (9.8–17.2%), H_2 (9.8–13.2%), CH_4, CO_2, H_2O and N_2 [4]. Subsequent combustion of this NH_3 can lead to the formation of an equivalent amount of NO_x, jeopardising all the advantages of the process.

The challenge for all those applications is to selectively oxidise NH_3 to the harmless product N_2 according to the following reaction:

$$2NH_3 + \tfrac{3}{2}O_2 \rightarrow N_2 + 3H_2O \qquad (2)$$

In the literature, various catalysts are reported to be active for this reaction. However, N_2 yields are generally below 80% over limited temperature ranges [5–7]. In a previous paper, we showed that γ-Al_2O_3-supported Ni, Fe and Mn catalysts can give rise to N_2 yields >90% [8]. However once again these systems display a limited operating temperature range.

Thus, it is clear that further improvements in reaction selectivity and of the temperature window are necessary. However, to achieve these goals we require a better understanding of the reaction mechanism. Two major routes have been proposed in the literature for the selective production of N_2 from the oxidation of NH_3. The first is the selective catalytic oxidation (SCO) of NH_3 to N_2 by a direct route based on the recombination of $2NH_x$ species giving rise to an hydrazinium intermediate H_xN–NH_x [9–11]. The other is the in situ or "internal" selective catalytic reduction (iSCR) and is a two-step mechanism and involves the oxidation of a significant percentage of the NH_3 into NO_x species. These interact with NH_3 molecules and are reduced to N_2 [12,13].

In this work, we have examined the adsorption and desorption characteristics of NH_3 and also NO and N_2H_4 as model reaction intermediates for the iSCR and SCO pathways, respectively. Temperature-programmed desorption (TPD) and oxidation (TPO) as well as diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) are used and correlated to develop a better understanding of possible reactions occurring.

2. Experimental

2.1. Catalyst and gases

The 10% Ni/Al_2O_3 catalyst was prepared by incipient wetness impregnation of an Akzo Chemie CK300 γ-Al_2O_3 support (extrudate form, S_{BET}=192 $m^2\,g^{-1}$ and particle size 250–600 μm) with an aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ (Fluka, Purum p.a., crystals, >99%). Calcination was carried out in static air at 700°C for 24 h.

Various gases: 1±0.02% NH_3/He (Air Products), 0.495% NO/He (BOC special gas, total NO_x=0.497%), O_2 (BOC zero grade) were used during the TPD, TPO as well as the DRIFTS experiments. The He was dried before use by molecular sieves (5A, BDH) during the in situ DRIFTS experiments. Hydrazine monohydrate $N_2H_4{\cdot}H_2O$ (Sigma, 64% hydrazine) was used as the source of N_2H_4.

2.2. Analytical procedures

TPReaction, TPD and TPO experiments were carried out in a conventional atmospheric pressure microreactor described elsewhere [8] with on-line MS analysis (Hiden DSMS). TPReactions were performed using 200 mg of catalyst. One thousand ppm of NH_3 (or N_2H_4) and 5% O_2, balance He was fed through the catalyst during the temperature ramp (10°C min^{-1}). N_2H_4 was introduced using a Hamilton syringe (250 μl) connected to a precision pump (Instech 2000). For the TPD/TPO experiments, 100 mg of catalyst was used. The sample was pre-treated in situ in 5% O_2/He at 600°C for 2 h prior to each experiment. After the dosing and flushing steps, the catalyst temperature was increased at a rate of 10°C min^{-1} from room temperature to 800°C.

Fragmentation patterns of N_2O (m/e=44) on the NO and N_2 signals, as well as H_2O (m/e=18) and NO_2 (m/e=46) on the NH_3 and NO signals, respectively, were determined and corrected. For experiments involving N_2H_4, m/e=32 and m/e=30 signals were used in the absence of O_2 and NO, respectively.

Adsorption and transient DRIFTS experiments were carried out with 100 mg of powdered catalyst using a Harrick heatable and evacuable cell. DRIFT spectra were recorded using a Perkin-Elmer 1720X Fourier Transform spectrometer (4 cm^{-1} resolution) equipped with a mercury–cadmium–telluride (MCT) detector.

The procedure used during the TPD/TPO experiments was the same as that reported for the mass spectrometry analyses. The spectrum backgrounds were recorded just after the pre-treatment during the temperature decrease by steps of 50°C (after 10 min of stabilisation and averaging 64 scans).

3. Results and discussion

3.1. NH_3 adsorption and reactivity

3.1.1. TPReaction

The TPReaction profile obtained on 10% Ni/Al_2O_3 is shown in Fig. 1. From the beginning of the temperature ramp, NH_3 desorbs from the catalysts contributing to the NH_3 signal in addition to the unreacted NH_3 fed into the gas stream. Above 350°C, NH_3 begins to react and gives rise mainly to N_2 and H_2O. NO and traces of N_2O are also formed. Finally, from the temperature range where full NH_3 conversion is reached (~650°C), the formation of N_2 is progressively replaced by the formation of NO.

These data are consistent with results obtained previously under steady-state conditions [8]. The additional analyses of N_2O by mass spectrometry confirm the good N_2 selectivities and yields reached with this catalyst.

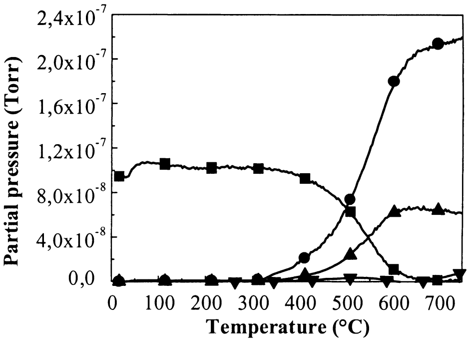

Fig. 1. TPReaction profile on 10% Ni/Al_2O_3 (1000 ppm NH_3, 5% O_2, balance He): (■) NH_3; (▲) N_2; (▼) NO; (●) H_2O.

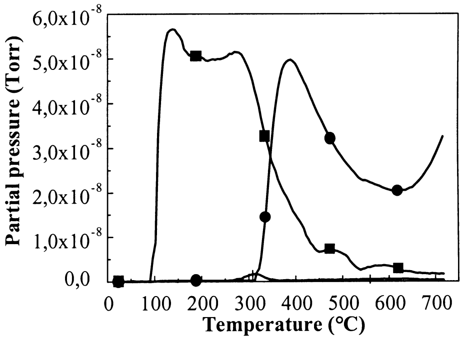

Fig. 2. TPD profile after adsorption of NH_3 on 10% Ni/Al_2O_3: (■) NH_3; (+) N_2O; (●) H_2O.

3.1.2. TPD

The TPD profile of NH_3 on 10% Ni/Al_2O_3 is shown in Fig. 2. NH_3 is seen to desorb from the catalyst over a broad temperature range (100–550°C). This is characteristic of the presence of several adsorbed NH_3 species differing in thermal stability [6–8]. Thus, in addition to the low temperature peak (100°C), the shoulder at 275°C indicates two major species on the surface of the Ni-based catalyst. Traces of N_2O are also detected at ca. 300°C, while H_2O desorbed from the catalyst only above this temperature. No trace of N_2 or NO are detected over the entire temperature range examined.

It should also be noted that no major change was observed when NH_3 was co-adsorbed with O_2. This is in accordance with results obtained by Kijlstra et al. [14].

3.1.3. TPO

The product profiles from NH_3 TPO are presented in Fig. 3. It can be seen that NH_3 desorbs in the same temperature range recorded in TPD, i.e. 100–550°C. The main desorption peak of H_2O and the small production of N_2O also occur at the same temperatures. However, it should be noted that increasing the temperature in an oxidative atmosphere gives rise to the formation/desorption of small amounts of N_2 in the temperature ranges 250–350°C and 400–500°C. In parallel, small quantities of H_2O were desorbed

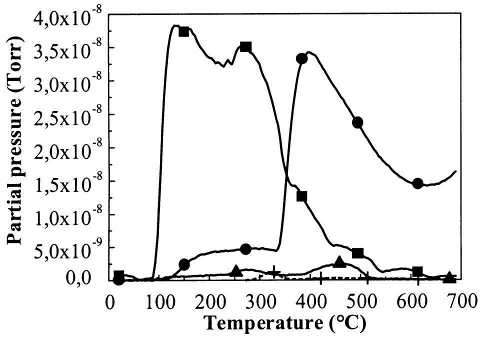

Fig. 3. TPO profile after adsorption of NH_3 on 10% Ni/Al_2O_3: (■) NH_3; (▲) N_2; (+) N_2O; (●) H_2O.

from 125 to 325°C before the main N_2 desorption peak. This suggests that gas phase O_2 is necessary to activate NH_3. However, this activation occurs at high temperatures where only small amounts of NH_3 are left on the surface.

The IR spectrum resulting from NH_3 adsorbed in presence of O_2 on the dried surface of the catalyst is reported in Fig. 4 (upper spectrum). The additional spectra presented below are recorded under TPO conditions. The two main bands observed at 1607–1626 cm^{-1} and 1230–1250 cm^{-1} are assigned to the asymmetric and symmetric deformation modes, respectively, of NH_3 co-ordinated on Lewis acid sites. The band at 1484 cm^{-1} and the shoulder at 1691 cm^{-1} are due to the asymmetric and symmetric deformation modes, respectively, of ammonium cations NH_4^+, resulting from the adsorption of NH_3 on Brønsted acid sites. The band at 1392 cm^{-1} was observed in similar conditions on the support alone: γ-Al_2O_3 by Kijlstra et al. [14]. However, no assignment was reported. According to the peak behaviour when the sample is heated, it may be assigned to NH_4^+ species on the support.

All these bands decrease in intensity when the temperature rises in the presence of O_2. Comparison with the TPD of NH_3 and the TPO of NH_3+O_2 (Figs. 2 and 3), the desorption of unreacted NH_3 and the activation of NH_3 are responsible for these decreases. These observations are corroborated by the appearance of new absorption bands (peak at 1546 cm^{-1} and shoulder at 1280 cm^{-1}) when the temperature reaches ca. 300°C. This corresponds to TPO conditions where only small amounts of NH_3 are left unreacted on the surface and neither NO nor NO_2 is observed desorbing from the surface. Thus, it is reasonable to assign these peaks to an intermediate of N_2 formation. In parallel, there is a corresponding decrease in the shoulder at 1508 cm^{-1}, a band which has been previously assigned to an amide (NH_2) surface species [14,15].

3.2. N_2H_4 adsorption

Hydrazine-type species have been suggested to be the intermediate involved in the direct formation of N_2 by SCO of NH_3 [9–11]. Thus, in this section, $N_2H_4 \cdot H_2O$ is used to model this intermediate.

3.2.1. N_2H_4 adsorption and effect of O_2

The IR spectrum of N_2H_4 adsorbed on the catalyst is presented in Fig. 5 (upper spectrum). It is composed

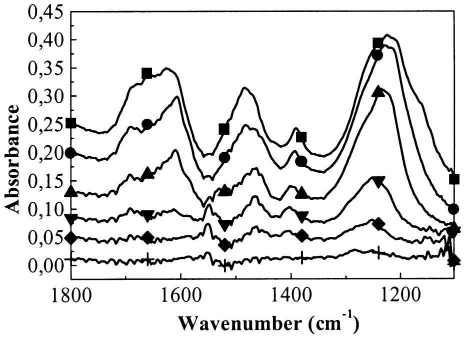

Fig. 4. IR spectra after adsorption of NH_3+O_2 on 10% Ni/Al_2O_3 followed by evacuation (■) and subsequent heating in O_2 to: (●) 100; (▲) 200; (▼) 300; (◆) 350; (+) 400°C.

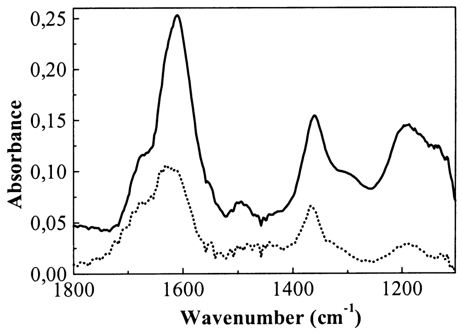

Fig. 5. IR spectra after adsorption of N_2H_4 on 10% Ni/Al_2O_3 followed by evacuation in Ar (—) and subsequent introduction of O_2 (- - -).

of three major peaks (1606, 1354 and 1182 cm^{-1}). According to Ref. [11] and relevant references therein, the first two bands can be assigned to NH_2 scissoring and NH_2 wagging deformation modes, respectively. The third band may be assigned to N–N stretching deformation mode of hydrazine. Other smaller peaks and shoulders are present at 1670, 1490, 1310 and 1125 cm^{-1}. These features will not be discussed in detail as they do not correspond to the bands arising under the conditions necessary for the formation of N_2. This is also true for the main absorption bands. Similarities with the spectrum of NH_3 are evident (1606 and 1182 cm^{-1}). However, this is not surprising since N_2H_4 is known to decompose under the present conditions into N_2 and NH_3 [16].

When O_2 is passed over the N_2H_4 pre-dosed catalyst at room temperature, all bands of absorption decrease, in particular, the band assigned to the N–N stretching deformation mode (1182 cm^{-1}). As expected, this shows the low stability of adsorbed N_2H_4 surface species under oxidative conditions.

3.2.2. TPO

The TPO of adsorbed N_2H_4 confirmed its low stability in an oxidative atmosphere (Fig. 6). H_2O desorbs in large quantities while only small amounts of N_2 desorb from 50°C with a maximum at 100°C. Also, no other product (NO, N_2O or NO_2) is formed over the entire temperature range.

According to these data, the decomposition of an hydrazinium-type intermediate into N_2 is not the limiting step of the reaction. This is in accordance with TPO data where the activation of NH_3 appears to be the slow step, notwithstanding any contribution of N–N recombination to the overall rate. However, the DRIFTS data show no evidence that an intermediate such as N_2H_4 is involved in the mechanism of formation of N_2.

3.3. NO adsorption and reactivity

A more oxidised type of species containing an oxygen atom has been suggested to be the intermediate involved in the formation of N_2 by in situ SCR mechanism [12,13]. Thus, in this section, NO is used to model this potential intermediate.

3.3.1. TPD

The TPD profile of NO co-adsorbed with O_2 exhibits two regimes of NO desorption (Fig. 7). Firstly, NO of low stability desorbs from 50 to 350°C. Traces of NO_2 also desorb at ~200°C. Secondly, a more stable type of NO species desorbs from 400 to 500°C giving rise to NO, NO_2 and O_2. This suggests the decomposition of nitrate-type surface species [16–17]. Traces of N_2 are also observed from the catalyst. However, it is the presence of potentially thermally stable nitrate-type species under normal reaction conditions, is an important result when one considers that the activation of NH_3 only begins at 350–400°C.

The IR spectra of NO adsorbed in the presence of O_2 and obtained in the conditions of the TPO experiment (Fig. 8) show the presence of several nitrite/nitrate surface species as suggested earlier. According to Kijlstra et al. [14], the main band at 1313 cm^{-1} as well as the shoulder at 1431 cm^{-1} can be assigned to

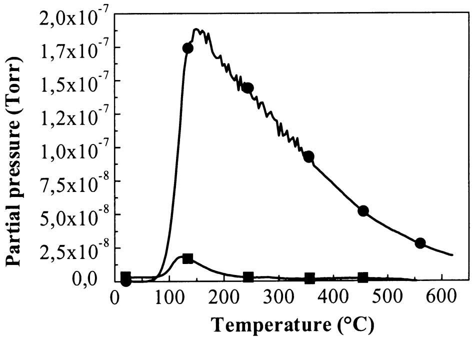

Fig. 6. TPO profile after adsorption of N_2H_4 on 10% Ni/Al_2O_3: (■) NH_3; (●) H_2O.

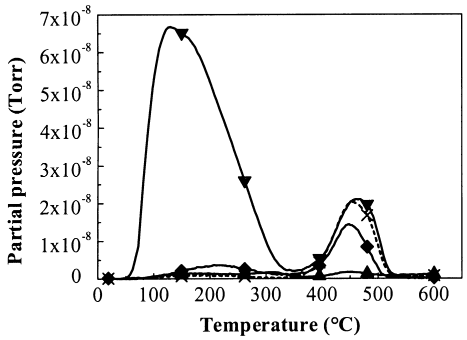

Fig. 7. TPD profile after adsorption of NO+O_2 on 10% Ni/Al_2O_3: (▼) NO; (◆) NO_2; (×) O_2; (▲) N_2.

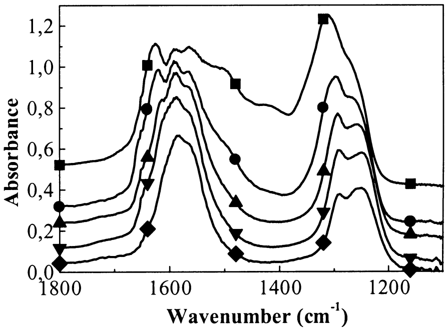

Fig. 8. IR spectra after adsorption of NO+O_2 on 10% Ni/Al_2O_3 followed by evacuation (■) and subsequent heating in O_2 to: (●) 100; (▲) 200; (▼) 300; (◆) 400°C.

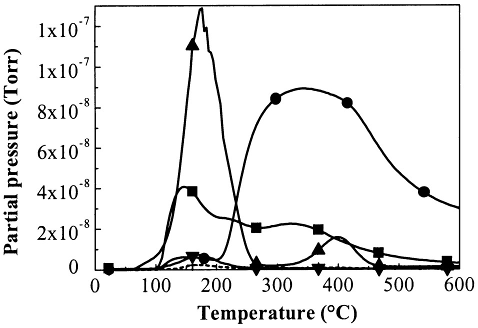

Fig. 9. TPD profile after adsorption of NH_3+NO+O_2 on 10% Ni/Al_2O_3: (▲) N_2; (●) H_2O; (■) NH_3; (▼) NO; (- - -) N_2O.

monodentate nitrite species. The bands between 1550 and 1600 cm^{-1} are due to bidentate nitrates of "type I" and "type II", respectively, according to the classification of Schraml-Marth et al. [18]. Finally, the band at 1625 cm^{-1} can be assigned to bridged nitrate species.

Upon heating, the band corresponding to the monodentate nitrite (1313 cm^{-1}) decreases. According to TPD this gives rise to a desorption of NO. It also results in a transformation of these surface species to bridged and bidentate nitrate species. Indeed, the bands from such species increase from room temperature to 100 and 350°C, respectively. This transformation is also illustrated by the shift of the monodentate nitrite band from 1313 to below 1290 cm^{-1} and by the formation of a new band at ~1250 cm^{-1} (also specific to bidentate nitrate species).

Finally, the bands corresponding to the most stable nitrate species begin to decrease above 350°C. This is in accordance with the TPD of NO+O_2 (Fig. 7). It is noteworthy that both bands (1546 and 1280 cm^{-1}), suggested to belong to the intermediate of the reaction of N_2 formation, correspond reasonably well to these stable nitrate species bands.

3.3.2. Reactivity with NH_3

The reactivity of NH_3 and NO is illustrated by the TPD of NH_3+NO+O_2 (Fig. 9). The three components were co-adsorbed on the surface of the catalyst. N_2 formation and desorption occurs in two temperature ranges 60–275°C and 325–475°C, with a maximum at ~170°C. The observation of N_2 at ca. 170°C may be due to the decomposition of ammonium nitrite. However, it does illustrate that N_2 formation can occur at lower temperatures than are required when NO is not co-adsorbed. As a result, NH_3 activation, or indeed oxidation of part of the NH_3 to NO_x appears to be the limiting step for selective NH_3 oxidation. This correlates with the poor redox properties of the catalyst reported previously [8] resulting in the comparatively high temperature necessary for the catalyst to become active (peak at ca. 400°C). Thus it appears that once NO is formed in situ, it reacts very quickly with unreacted NH_3 species on the surface. It is noteworthy that when NO and NH_3 are co-adsorbed, only very small amounts of NO desorb unreacted from the catalyst. This can explain partly the very high selectivity of N_2 observed on this catalyst.

The temperature ranges of N_2 formation seem to correspond to the ranges of NO desorption observed during the TPD of NO+O_2 (Fig. 7). This may suggest that NO (and/or NO_2) needs to be in the gas phase to allow the N–N recombination. The fact that no trace of NO_2 is observed under these conditions may also suggest that the in situ SCR can occur with both NO and NO_2 or with various nitrate/nitrite surface species. However, the TPO of NH_3 (Fig. 4) suggests that under the reaction conditions, only bidentate nitrates are formed from NH_3.

3.3.3. Summary

1. Under the conditions of the NH_3 TPO, the formation of a new surface species is observed by DRIFTS (bands at 1546 and 1280 cm^{-1}). The temperature range at which this occurs corresponds to the temperatures required for N_2 for-

mation. These bands are assigned to the reaction intermediate(s).

2. The study of N_2H_4 as a model intermediate gives no evidence that the SCO of NH_3 occurs via direct recombination of NH_x species via a hydrazinium-type moiety. Neither the thermal behaviour nor the IR bands correspond to the studied reaction.
3. The study of NO as a model of intermediate reveals good correlations between the observed bands and the bidentate nitrate species (type II), which also reveals to be a more stable species. This presents strong evidence that the reaction occurs by the in situ SCR mechanism.
4. The reaction between NO and NH_3 is shown to be very fast on the surface of the catalyst. This suggests that NH_3 activation is the limiting step of the process. Once an NH_3 molecule is oxidised into an NO species, the second reaction of SCR is faster than the desorption of NO. This concurs with the hypothesis that the species observed during the NH_3 TPO is the intermediate of the reaction. Indeed, under these conditions, very small amounts of NH_3 are left on the surface, limiting the consumption of the intermediate. This is possibly due to the high intrinsic thermal stability of the intermediate.

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