

## Transient *operando* study on the NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> interplay in V-SCR monolithic catalysts

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### 1 Abstract

The assessment of an integral catalytic reactor facilitating *operando* spectroscopic measurements on a monolith has been carried out using NH<sub>3</sub>-SCR on a vanadia-based catalyst as a probe reaction. The NH<sub>3</sub>-SCR mechanism is revisited by studying the adsorbed ammonia and ionically bound ammonium ions and their relations to Lewis and Brønsted acid sites during reaction. The simultaneous presence of molecular water and ammonia adsorbed on the surface is intrinsic to low temperature NH<sub>3</sub>-SCR, and their IR absorption bands overlap in the bending region around 1600 cm<sup>-1</sup>. This has to be tackled in order to genuinely reproduce real reaction conditions and simultaneously extract relevant spectroscopic data of a working industrial monolithic catalyst. This *operando* study on a V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-sepiolite monolith is performed without added water in the gas phase, but water formed upstream is adsorbed further down, and thus detected by FTIR spectroscopy. We observed that Multivariate Curve Resolution Alternating Least Squares (MCR-ALS) analysis of the 1620 cm<sup>-1</sup> envelope of peaks can successfully resolve the bands of adsorbed H<sub>2</sub>O and NH<sub>3</sub> in the monolith during transients between NH<sub>3</sub> and NO + O<sub>2</sub> flow. Their evolution along with that of surface ammonium ions indicates that generated water hydrolyzes molecularly dispersed vanadia species of the catalyst creating new Brønsted acid sites, and that adsorbed ammonia is either used for the SCR reaction, or converted into the ammonium ion, which then participates in the SCR reaction.

### 2 Keywords

V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-sepiolite honeycomb; NH<sub>3</sub>-SCR; *operando* FTIR; acid sites; MCR-ALS

### 3 Introduction

NH<sub>3</sub>-SCR (selective catalytic reduction with ammonia), Eq. 1, has been widely employed in the industry since 1970 for removal of NO from off-gases:



The commercial catalyst for all type of industrial SCR applications is a monolith based on tungsta-promoted vanadia supported on titania anatase. The monolithic structure combines excellent gas-solid contact conditions with low pressure drop, whereas the V-based active phase exhibits superior performance/price ratios, low N<sub>2</sub>O selectivity, and unrivaled sulfur deactivation resistance compared to other types of catalysts. Despite being a well-established technology, research on SCR has regained interest in the recent years due to the many new legislative-enforced applications for NO<sub>x</sub> abatement technology in medium and smaller units like incinerators, FCC regenerators, cement factories, automotive applications, etc. Moreover, the reaction mechanism is still heavily debated, partly due to the rise of zeolite-based automotive applications, but also due to continued interest in understanding the traditional but still controversial vanadia/titania-based catalytic cycle.[1-13]

The vanadium coverage of the commercial catalysts is below the dispersion limit ("monolayer") of 6-7 atom/nm<sup>2</sup> to avoid the formation of crystalline V<sub>2</sub>O<sub>5</sub> and obtain molecularly dispersed vanadium oxide species, strongly stabilized by the V-O-Ti bonds formed upon titration of the support hydroxyl groups, which is also apparent for other supported oxides.[14, 15] Surface vanadium oxide species are isolated at low coverage, but progressively polymerized by formation of V-O-V bonds as the coverage increases.[16-18] Progressive hydroxylation models obtained by DFT and molecular dynamics calculations describe for typical experimental conditions hydroxylated structures for supported vanadia that unlike the dehydrated one (stable only in the absolute absence of humidity, *i.e.* under high vacuum) provide a simple rational explanation for the co-existence of redox and Brønsted acid sites in supported vanadia species. They further account for the evolution of the vanadyl (V=O) Raman mode with temperature and humidity, which is observed by *in situ* spectroscopy for both isolated[19] and polymerized[20] vanadium oxide species on titania.[21].

The states of supported vanadia during NO<sub>x</sub> SCR at 200-300 °C will thus be strongly affected by coordination of water, a ubiquitous molecule. Fuel combustion generates water along with the undesired NO<sub>x</sub>. In addition, the SCR reaction between NH<sub>3</sub> and NO<sub>x</sub> leads to the formation of N<sub>2</sub> and H<sub>2</sub>O. The actual initial interaction of NH<sub>3</sub> with molecularly dispersed vanadia, its interplay with water and, finally, with NO<sub>x</sub> species is still a subject of debate.

Important progress in understanding the surface chemistry of vanadia-based SCR (V-SCR) systems was observed in the 1990's, especially with *in-situ* and *operando* FTIR and Raman spectroscopic studies.[3, 21-25] However, remarkable differences in opinions about the mechanism prevail.[9, 11] It is generally recognized that both adsorbed ammonia on oxo vanadia Lewis acid sites and ammonium ions associated with Brønsted acid sites are

precursors to an activated site that can selectively reduce weakly adsorbed NO via an Eley-Rideal type mechanism, at least at medium-high temperatures.[21-24, 26, 27] Water appears to shift the equilibrium between  $\text{NH}_3$  and  $\text{NH}_4^+$  species adsorbed on the catalyst surface, and thus the ratio between Lewis and Brønsted acid V-O sites depends on the gas phase humidity; this imposes a strong influence of the experimental conditions on the observations reported in the literature.

The most successful tool for distinguishing adsorbed sites on a catalytic surface is FTIR spectroscopy, which probes the different N-H bending modes in the mid IR (MIR) region, and yields different band positions for  $\text{NH}_4^+$  compared to  $\text{NH}_3$ . The development of advanced *operando* techniques is forming a new base for studying the system more in detail and in realistic conditions. We have demonstrated the viability of *operando* spectroscopic analyses of structured catalysts in their final shape using transmission FT-IR[28] and Raman[29] spectroscopies. Here we test our monolithic FTIR *operando* cell with a working honeycomb catalyst composed by V-W-TiO<sub>2</sub>-sepiolite. We aimed at demonstrating that the interrelation between Brønsted and Lewis sites can be observed by implementing the *operando* concept on monolithic catalysts combined with state-of-the-art multivariate data analysis software. For this purpose, we have designed an experiment in the integral monolithic reactor without added water in the gas phase, so that water formed upstream in the monolith is adsorbed further down, and then detected by *operando* FTIR spectroscopy. During a reaction sequence, with NO and O<sub>2</sub> titrating the catalyst surface for pre-adsorbed ammonia, it can be seen how it is either directly used for the SCR reaction, or converted into the ammonium ion, which then participates in the SCR reaction. We obtain valuable information on secondary effects from the water produced upstream, which is complementary to other more fundamental and direct observations performed on kinetically restricted pelletized or powdered catalysts. It is not the intention of this work to enter a detailed discussion of the  $\text{NH}_3$ -SCR mechanism in itself, but rather revisit the mechanism by studying the adsorbed ammonia and ionically bound ammonium ions and their relations to Lewis and Brønsted acid sites during reaction.

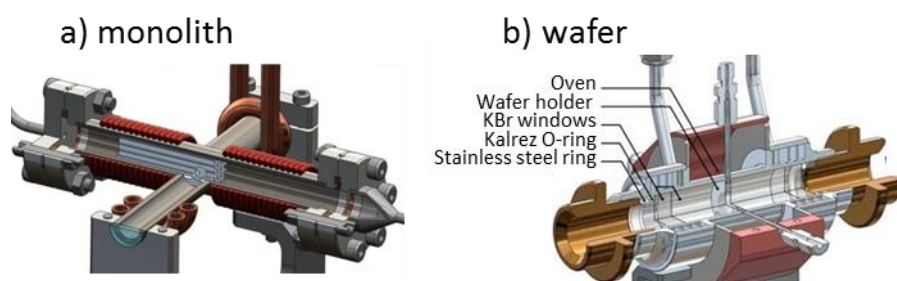
## 4 Experimental

### 4.1 Catalyst preparation

A V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub>-based  $\text{NH}_3$ -SCR monolithic catalyst similar to the industrial type (3% V<sub>2</sub>O<sub>5</sub>) was prepared by extrusion of a paste containing pre-tungstated high surface area titania as support (DT-52, CristalACTIV™, contains 10 wt.% WO<sub>3</sub>, 1.35 wt.% SO<sub>3</sub>), natural silicates as binder (Pansil 100, Tolsa S.A., 60 wt.% sepiolite), and  $\beta$ -VOSO<sub>4</sub>·5H<sub>2</sub>O as vanadia precursor. The dye employed produced 12-channel honeycomb monoliths with 100 squared channels per square inch (cpsi), a wall thickness of 0.92 mm and a channel width of 1.7 mm. After drying and calcination at 773 K the final monolith had a geometric surface area of 991 m<sup>2</sup> m<sup>-3</sup>, and a specific surface area ( $S_{\text{BET}}$ ) of 112 m<sup>2</sup> g<sup>-1</sup>. [28]

### 4.2 *Operando* FTIR-MS setup

The experimental set-up is composed of four main parts: 1) the gas flow set-up that introduces the gas mixture into the lines (heated at 60 °C); 2) the *operando* reactor-cell, either for monolith[28] or for wafer[30] samples, shown in **Figure 1**; 3) the infrared spectrometer, used to probe the catalyst surface (Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with a MCT detector); and 4) the exhaust gas analysis system, employed to follow the gas phase changes, comprised by a quadruple mass spectrometer (Pfeiffer Omnistar GSD 301, 1 s time-resolution) and a gas micro-cell coupled to the FTIR spectrometer. The mass flow controllers set can prepare two gas mixtures and send them by independent heated lines to the reactor-cell; one was used for *activation* (O<sub>2</sub>/Ar) or *saturation* (NH<sub>3</sub>/Ar), and the other one for *reaction* (NO/O<sub>2</sub>/Ar with or without NH<sub>3</sub>). More details about the IR *operando* setup can be found elsewhere.[30, 31]

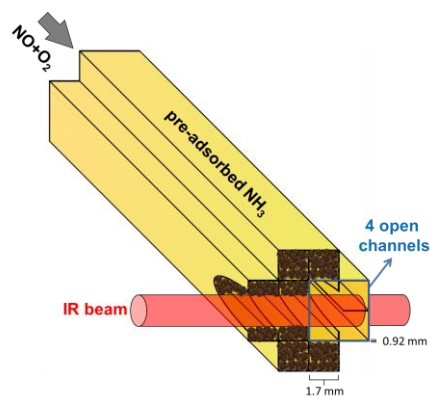


**Figure 1.** FTIR *operando* reactor-cells for a) monolithic[28] or b) self-supported pelletized[32] catalysts.

The *operando* system was operated in two different configurations: one for monoliths, to study NH<sub>3</sub>-SCR with structured catalysts in the industrially relevant final shape, and one for pellets (sandwich cell), which facilitates more fundamental studies, mainly due to the higher time resolution and better fluid dynamic properties.

#### 4.3 NH<sub>3</sub>-SCR *operando* studies on a monolithic catalyst

The IR reactor-cell designed to study monolithic catalysts under *operando* conditions consists of a cylindrical reaction chamber of ½ inch size surrounded by an electronically controlled oven. The reactor-cell is crossed by a probe channel surrounded by an air cooling system and closed by optical windows (KBr). A piece of monolith was cut into the size of the monolithic IR cell (L = 3.5 cm), and a distribution cone and quartz wool were used to keep it in place and favor the gas diffusion at the entrance of the monolithic channels. In order to monitor the shaped catalyst by transmission FTIR spectroscopy a small hole was drilled through the monolith in the direction of the IR beam; only one wall was left, and polished to such a thickness that IR transmission was feasible, ca. 300 μm (see **Figure 2**). The hole was drilled as close as possible to the downstream end of the monolith



**Figure 2.** Monolith with hole for FTIR beam with last wall left as ca. 300  $\mu\text{m}$  transparent IR sample.

In order to achieve a gas hourly space velocity (GHSV) of  $3300\text{ h}^{-1}$ , relevant for industrial conditions (area velocity =  $3.3\text{ Nm h}^{-1}$ ), 8 of the 12 channels were plugged with inert SiC. The catalyst was first activated at  $400\text{ }^\circ\text{C}$  in  $10\% \text{ O}_2/\text{Ar}$  and then submitted to two-step  $\text{NH}_3$ -SCR experiments performed at 200, 250 and  $300\text{ }^\circ\text{C}$ . In the first step, of ammonia adsorption, a  $1000\text{ ppm NH}_3/\text{Ar}$  flow was fed to the oxidized catalyst until saturation at the reaction temperature. After a 30 min purge in Ar the catalyst was then exposed to  $1000\text{ ppm NO}$  in Ar flow with  $3.5\% \text{ O}_2$ . IR spectra were collected as average of 256 scans.

#### 4.4 $\text{NH}_3$ -SCR *operando* studies on pelletized catalyst

The monolithic sample was crushed and pelletized at  $0.8\text{ ton cm}^{-2}$  in order to perform FTIR spectroscopy in the *operando* set up with the “sandwich reactor-cell”.<sup>[30]</sup> The catalyst was first activated at  $450\text{ }^\circ\text{C}$  in  $10\% \text{ O}_2/\text{Ar}$ . The study was performed at  $310\text{ }^\circ\text{C}$  with  $1000\text{ ppm NH}_3$ ,  $1000\text{ ppm NO}$ , and  $3.5\%$  oxygen (argon as balance) at a constant area velocity of around  $3.3\text{ Nm h}^{-1}$ . IR spectra were collected as average of 16 scans at a time resolution of 1 spectrum per 2.65 seconds.

#### 4.5 Chemometrics

The IR absorption bands of adsorbed ammonia and molecular water around  $1600\text{ cm}^{-1}$  were resolved using commercial software PEAXACT (S-PACT GmbH) to perform multi component analysis (Multivariate Curve Resolution Alternating Least Squares, MCR-ALS) of the spectra and obtain an un-biased, physically motivated, quantitative, mathematical model of the surface species.<sup>[33]</sup>

## 5 Results and Discussion

### 5.1 Technical challenges tackled in this study

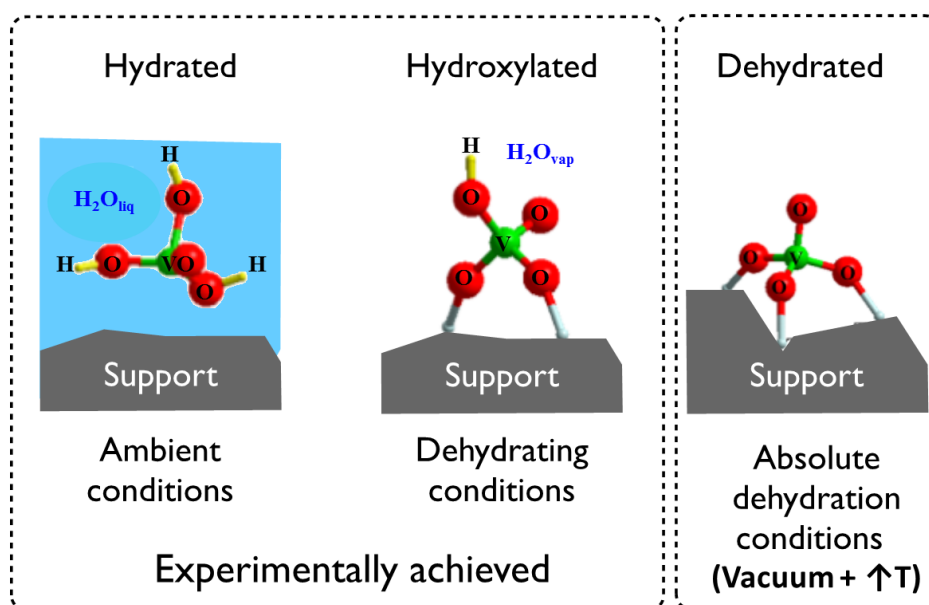
The *operando* reactor-cell for pelletized samples (sandwich cell) is adequate for fundamental studies due to the high time resolution and good fluid dynamic properties attained. Moreover, a pelletized catalyst in essence represents a model system for a bulk monolith in the sense that it is a thin wall of catalyst in steady state equilibrium with the gas passing by. However, the differences among pelletizing, coating and shaping methods related to pressure (porosity), binders and additives (composition), catalyst-support interface (interaction), etc. may significantly affect the experimental results obtained. This is the motivation for extending the *operando* methodology into monoliths.

The commercial catalyst for all type of industrial NH<sub>3</sub>-SCR applications is a monolith based on tungsta-promoted vanadia supported on titania anatase. Here we test in our monolithic FTIR *operando* reactor-cell a bulk V-W-TiO<sub>2</sub>-sepiolite honeycomb catalyst with the industrially relevant final composition and shape, even though (or rather especially since) as coextruded catalyst it inherently contains components such as binders, traces of rheological additives, etc., which change the game when assessing structure and reactivity. The hole needed for IR transmission through the monolith was drilled as close as possible to the downstream end to ensure that the state of the monolithic catalyst probed by the IR beam can be correlated to the environment described by the gas composition monitored at the reactor outlet, which, however, is a result of the catalytic activity of the whole reactor, not just the final part. The modification of the monolith does not affect the surface composition, because the active phase was incorporated to the bulk before the monolith extrusion and not just wash-coated, but might slightly change the catalytic efficiency at the exact spot where the IR beam passes due to the reduction of the wall thickness. However, the system employed is probably the closest to industrially relevant conditions currently achievable.

## 5.2 Mechanistic challenges tackled in this study

The complexity of IR spectroscopic observations of the V-SCR system lies in the variety of species involved with similar and overlapping signals. Up to five different adsorption modes of NH<sub>3</sub> on metal oxides have been defined in the literature:[34] (i) H-bonded to surface O or OH, (ii) H-bonded through N to surface OH, (iii) Lewis-acid-bonded to electron-deficient metal, (iv) Brønsted-acid-bonded with formation of NH<sub>4</sub><sup>+</sup>, (v) dissociation with NH<sub>2</sub> or NH bonded to the metal and formation of OH group. Moreover, several polymeric and monomeric species are possible for the supported vanadia on the catalyst, both as tetrahedral (101 and 100 facets of anatase) or octahedral (001 facet of anatase) structures, and reduced or oxidized forms alternate during the catalytic cycle. In any case, the completely dehydrated structure of titania-supported vanadia with pure Lewis acidity (**Figure 3**, right) is stable only under high vacuum. Progressive hydroxylation models for supported vanadia species that have been validated by experimental observations and DFT and molecular dynamics calculations indicate that even small amounts of water molecules will adsorb dissociatively, hydroxylating the titania support and hydrolyzing the V-O bonds, thus leading to the co-existence of Lewis and Brønsted acid sites (**Figure 3**, middle). Temperature and humidity conditions modulate the Lewis/Brønsted

ratio up to the eventual total solvation of the vanadia species by molecular adsorption of water (Figure 3, left).



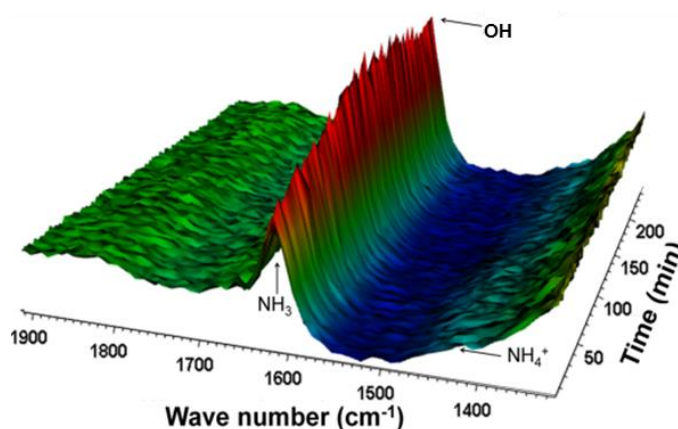
**Figure 3.** Molecular states of supported monomeric vanadium (V) oxide model species.

Hydrated solvated species dominate in ambient conditions,[18, 35] while in the initial dehydrated conditions of this study stable hydroxylated vanadium oxide species are expected to predominate, possessing for V(V) two V-O-Ti bonds, one V-OH bond and a V=O double bond.[9, 19, 20, 36] Thus, a variety of IR absorption bands could be observed. The spectra of the V-W-TiO<sub>2</sub>-sepiolite monolith, however, though containing essential information, are less informative than those of a V-W-TiO<sub>2</sub> powdered catalyst, because the bands are, in general, much less resolved (see Figure 5 in ref. [28]) This is caused by the thickness of the monolith and the extensive use of clay as binding material, which saturates the detector and increases the amount of adsorbed water. In particular, the -OH region around 3500 cm<sup>-1</sup> is saturated, as well as the region below 1300 cm<sup>-1</sup>. Thus, not only the band at ca. 1250 cm<sup>-1</sup> related to adsorbed ammonia on Lewis acid sites cannot be detected, but the main ammonia stretching vibration bands and the M-OH bands (M = metal: V, W, Ti, Si, Mg, Al) in the higher wavelengths region cannot be monitored either. Anyway, it is important to note that N-H IR absorption bands monitoring during transient experiments without isotopic labeling cannot differentiate the reactivity of the vanadia active phase and the tungsta promoter phase, although the surface hydroxylation induces significant Brønsted acidity on both types of surface sites.

### 5.3 Monolithic catalyst transition from ammonia to NO+O<sub>2</sub> flow conditions

**Figure 4** shows the region of interest of the FTIR spectra of the V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub>/sepiolite monolith surface obtained at 250 °C during the SCR reaction of gaseous NO+O<sub>2</sub> feed with pre-adsorbed ammonia. At the beginning of the series, *i.e.* on the ammonia-saturated catalyst, various bands are detected in the MIR region. Bending vibrations of adsorbed NH<sub>4</sub><sup>+</sup>, generally

considered as one of the main intermediates in the SCR reaction,[3, 22, 23, 26] are observed in the 1435-1450  $\text{cm}^{-1}$  range ( $\delta_{\text{as}}\text{NH}_4^+$ ).[37] This band, associated to the Brønsted acid sites, decreases as the reaction with NO proceeds until complete depletion. The assignment of the band at 1600-1650  $\text{cm}^{-1}$  can be misleading, because the deformation frequency of adsorbed molecular water ( $\delta\text{OH}$ ), at ca. 1620  $\text{cm}^{-1}$ , is superimposed with that of coordinated ammonia in Lewis acid sites ( $\delta_{\text{as}}\text{NH}_3$ ), at ca. 1610-1620  $\text{cm}^{-1}$ . [2, 13, 38, 39] The band is observed at any time: it is already present in the ammonia saturated surface, and increases and slightly blue-shifts over reaction time when the gas composition is switched from  $\text{NH}_3$  to  $\text{NO}+\text{O}_2$ , which essentially reflects the surface rehydroxylation by the water generated in the SCR reaction.

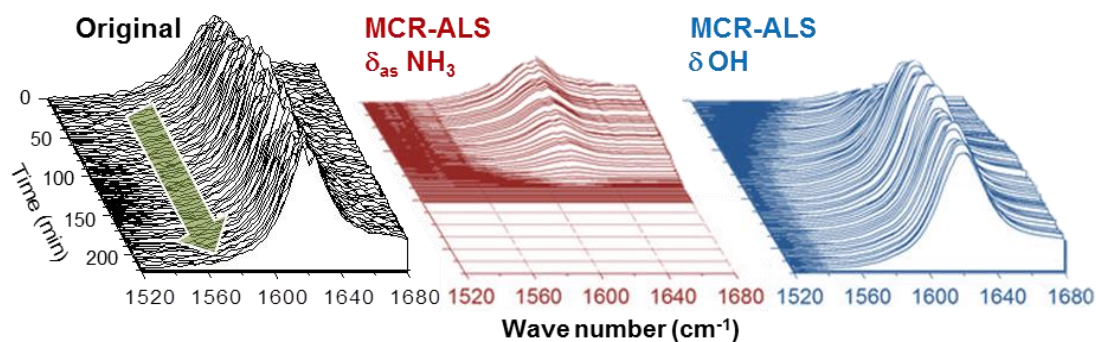


**Figure 4.** FTIR spectral series during reaction of 1000 ppm NO + 3.5 %  $\text{O}_2$  with pre-adsorbed ammonia over a  $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ /sepiolite monolithic catalyst at 250 °C.

The contribution of OH and  $\text{NH}_3$  to the band at 1600-1650  $\text{cm}^{-1}$  prevents the monitorization of the evolution of the adsorbed ammonia on Lewis acid sites without further treatment of the spectral information. Thus we used PEAXACT commercial software to resolve the convoluted peak over the transient and disclose the species contributions by implementing a multi-component regression analysis for the series of spectra given in **Figure 4**. The signal can be represented by two components, one decreasing and one increasing, assigned to adsorbed ammonia and water, respectively. The information contained in **Figure 4** was used to assess the results of the multi-component regression analysis: On the one hand, before feeding  $\text{NO}+\text{O}_2$ , the ammonia species are adsorbed on the  $\text{NH}_3$ -saturated surface on both Lewis and Brønsted acid sites; on the other hand, at the end of the transient period (240 min), when steady state is reached, all forms of adsorbed ammonia are depleted, because ammonia is not supplied in the gas feed and the surface has been titrated by  $\text{NO}+\text{O}_2$ . Hence, at this point, the ammonium ion peak initially observed at 1435  $\text{cm}^{-1}$  has disappeared and the peak formed by the combination of the signals of adsorbed water and ammonia has increased and is slightly blue-shifted from its initial position at ca. 1615  $\text{cm}^{-1}$  to the final position at ca. 1620  $\text{cm}^{-1}$ , reflecting the change in speciation. After ammonia depletion the peak must be assigned to  $\delta\text{OH}$ . The 3D plots of **Figure 5** display the time evolution of the as-obtained IR spectra in the 1520-1680  $\text{cm}^{-1}$



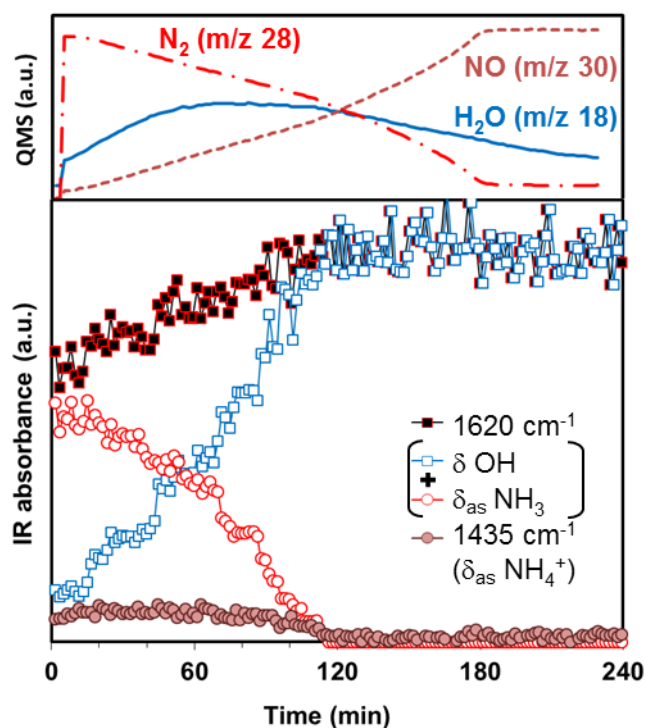
<sup>1</sup> region and the components calculated by the mathematical model corresponding to the vibrations of H<sub>2</sub>O and NH<sub>3</sub> adsorbed on Lewis acid sites.



**Figure 5.** *Operando* FTIR spectra during SCR of NO at 250 °C with pre-adsorbed ammonia. As obtained (left) and components after deconvolution by MCR-ALS: adsorbed ammonia on acid sites (middle) and hydroxyl bending mode (right).

The deconvolution performed with the MCR-ALS method is in accordance with the initial presence of ammonia adsorbed on Lewis acid sites and its gradual disappearing, as well as with water originating from the SCR reaction contributing to the progressive formation of the -OH band, so it was possible to model hydroxyl and ammonia spectral contributions. The NO+O<sub>2</sub> mixture consumes the adsorbed ammonia during the experiment up to total depletion. It is evident that on the V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub>-sepiolite monolithic catalyst ammonia molecules adsorbed on Lewis acid sites are present alongside ammonium ions adsorbed on Brønsted acid sites. Both are consumed during the SCR reaction and meanwhile the surface is continuously being hydroxylated as long as there is ammonia on the surface for the SCR reaction to form water.

**Figure 6** illustrates the relative evolution under reaction flow of the mass traces of the main gaseous species: H<sub>2</sub>O (*m/z* = 18), N<sub>2</sub> (*m/z* = 28) and NO (*m/z* = 30); and the FTIR bands of the main surface-bound species: convoluted and deconvoluted  $\delta$ OH and  $\delta$ NH<sub>3</sub> bands at ca. 1620 cm<sup>-1</sup>, and  $\delta$ NH<sub>4</sub><sup>+</sup> at 1435 cm<sup>-1</sup>.



**Figure 6.** *Operando* FTIR-MS results as a function of time during NO+O<sub>2</sub> reaction with surface-bound, pre-adsorbed NH<sub>3</sub> at 250 °C. Top: mass traces evolution in the reactor outlet. Bottom: evolution of surface species IR bands.

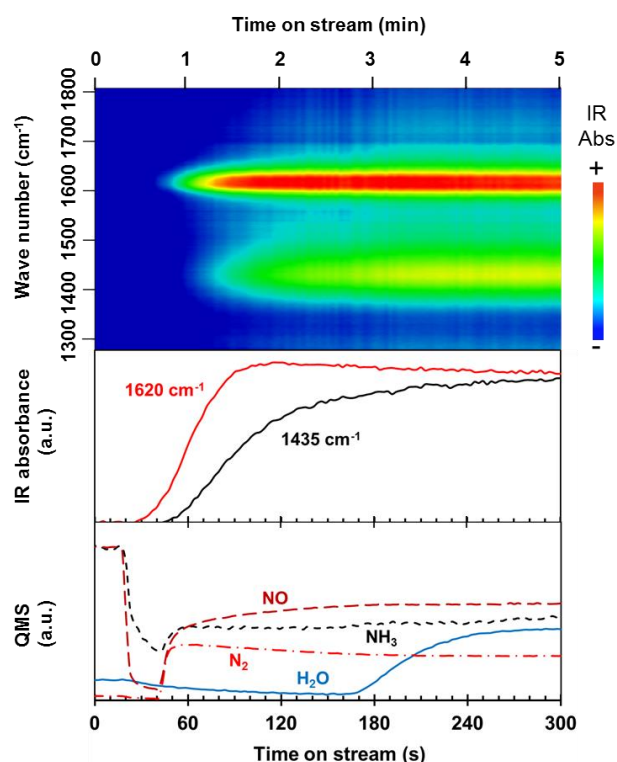
The data help to envisage the interplay between the pre-adsorbed species, ammonia and ammonium ion. While the calculated band of NH<sub>3</sub> bending vibrations at Lewis acid sites continuously decreases, a small but significant dynamic increase of the band at 1435 cm<sup>-1</sup>, assigned to the vibrations of the ammonium ions at Brønsted acid sites, is produced during the first 30-40 minutes of NO+O<sub>2</sub> feed. This effect is confirmed when the experiment is run at 200 °C (not shown), and a similar phenomenon was also reported by Lietti et al. with a pelletized catalyst.[40] The ammonium ion surface concentration increase has to occur at the expense of the Lewis acid bound ammonia population. Moreover, it must be related to the formation of new Brønsted acid sites by hydroxylation, because the surface was saturated with ammonia at the start of the transient. The local maximum of H<sub>2</sub>O in the outlet gas stream (at around 60 min) and the continuous decrease of N<sub>2</sub> and inverse increase of NO confirm that part of the generated water remains inside the reactor adsorbed on the catalyst surface. Accordingly, the calculated δOH band continuously grows until all ammonia species adsorbed on both the Brønsted and Lewis acid sites are consumed, which happens after 120 min under reaction flow, and thus SCR of NO is stopped and no more H<sub>2</sub>O is generated. When the experiment is run at 200 °C, the complete depletion of ammonia species is observed by FTIR to take place later, after 240 min under NO+O<sub>2</sub> flow (not shown). The higher the temperature, the lower the amount of total adsorbed ammonia and the faster the reaction rate; consequently, for the same V-SCR monolith under NO+O<sub>2</sub> flow the IR absorption bands of the surface-bound ammonia species disappear before at 250 °C than at 200 °C.

At 250 °C the traces of N<sub>2</sub> gaseous product are observed in the reactor outlet until min 180. The time gap between the evolution of N<sub>2</sub> and the surface species (**Figure 6**) is probably related to the reactor design. The amount of adsorbed ammonia available at the IR measuring point, with reduced thickness (see 4.3), is lower than for the rest of the monolith. At 300 °C this phenomenon becomes negligible due to the faster kinetic and diffusion rates and lower adsorption, and a near perfect match between *operando* IR bands and mass traces is observed.[28] This does not affect the conclusions of the current study on the existence of a Lewis acid sites band hidden under the adsorbed water band and the interplay between ammonia species bound to Lewis and Brønsted acid sites during SCR on a monolith.

According to the MS data NO appears in the outlet almost immediately, so the slower initial reduction of the NH<sub>3</sub> band in the IR spectra, collected at the downstream end of the monolith, is in agreement with the idea that in the first minutes of reaction NH<sub>3</sub> is mostly consumed on the first part of the monolithic bed, and thus the water that is converting Lewis into Brønsted acid sites by hydroxylation of surface vanadia species (probably) might be formed, at least partially, upstream. Later the decrease of the ammonia band is accelerated, as upstream ammonia is progressively consumed and more and more water reaches the tail end of the monolith. The concentration of surface ammonium species does not clearly change until most of the adsorbed ammonia disappears. So, at a first glance, apparently Brønsted sites are not being consumed during SCR reaction and only Lewis acid sites are involved in the reaction. But the IR bands evolution may also reflect that Brønsted acid sites are directly involved in the reaction and Lewis acid sites remain as a reservoir, being the rate of ammonium species consumption slower (or equal) than the rate of their replenishment from Lewis site bonded ammonia. In any case, DFT analysis shows that the particular identity of the ammonia species is not relevant for the rate of NO reduction.[12]

#### 5.4 Pelletized catalyst transition from oxidizing to NH<sub>3</sub>-SCR flow conditions

In order to shine further light on these relations an experiment was carried out with the same catalyst but as a pelletized sample in the low dead volume "sandwich cell",[41] which has very high time resolution. Instead of studying the decay of ammonium sites we looked at the transient from oxidized state to steady state SCR conditions for several runs. The evolution of the catalyst surface and the gas phase in the second run are given in **Figure 7**. The feed is switched from O<sub>2</sub>/Ar to SCR mix after 15 s. The water profile (*m/z* = 18) seems slightly decreasing under the reaction feed, which might be due to some residual humidity in the gas or to a background change in the MS when switching from oxidative to reducing feeds. However, this does not change the comprehension of the experiment, because the changes in the profile induced by the chemical reaction are significantly more intense.



**Figure 7.** Transient from 20% O<sub>2</sub>/Ar to SCR at 313°C (second run) highlighting the formation of NH<sub>3,ads</sub> and NH<sub>4</sub><sup>+</sup>. **Top:** FTIR spectra contour plot in the N-H bending region showing the growth of ammonia-derived species on the catalyst surface. **Middle:** surface species area profiles taken from the contour plot. **Bottom:** gas phase evolution of NH<sub>3</sub> (m/z 15, x20), H<sub>2</sub>O (m/z 18), N<sub>2</sub> (m/z 28) and NO (m/z 30).

It is worth noting that the NH<sub>3,ads</sub> band at 1620 cm<sup>-1</sup> can already be detected after 9 s exposure to the SCR gas (at t = 29 s) while the formation of NH<sub>4</sub><sup>+</sup> at 1435 cm<sup>-1</sup> first occurs at t = 42 s, which coincides with the first appearance of NO and NH<sub>3</sub> reactants and N<sub>2</sub> product. Therefore, adsorbed NH<sub>3</sub> is formed 12 s before any measurable reaction is observed, which may suggest (even if the system is not in the reaction conditions *sensu stricto*) that in very dry conditions the SCR reaction is auto-accelerated by the formation of Brønsted acid sites from product water. This idea is reinforced by the fact that water appears in the gas stream once the hydroxylation to form the Brønsted acid sites reaches a steady state, confirming that part of the generated water remains inside the reactor, as concluded in the monolithic test. At that moment ammonia starts to appear in the gas phase as well. We are currently studying ways to completely discriminate between spectator and active Lewis and Brønsted sites by performing isotopic exchange reactions with <sup>15</sup>NH<sub>3</sub>.

The main observation from this experiment in relation to our monolith studies is that NH<sub>4</sub><sup>+</sup> adsorbed species appear later than NH<sub>3,ads</sub> and are formed upon surface partial hydroxylation by water from the SCR reaction, as can be seen in Figure 6. Furthermore, in a monolithic reactor

the water formed upstream yields extra challenges in separating the  $\text{NH}_{3,\text{ads}}$  component from the water peak at  $1620\text{ cm}^{-1}$ .

## 6 Conclusions

A recurrent problem in experiments performed under realistic wet conditions is that the IR band from adsorbed water around  $1600\text{ cm}^{-1}$  overlaps with the band from ammonia adsorbed on the Lewis acid sites, which therefore apparently will show no clear correlation with SCR activity. Under these conditions the ammonium ions associated with Brønsted acid sites (from hydrous vanadia) will appear to dominate the SCR reaction. At laboratory scale, a commonly employed solution to avoid interferences in the IR signal by water is to dehydroxylate the pelletized (transmission) or powdered (diffuse reflectance) catalytic system by exposing the sample to high temperature and evacuation of the sampling chamber. However, investigations performed under controlled dry conditions tend to bias the discussion towards the importance of the Lewis acid sites, because the dominance of anhydrous vanadia is promoted. Further, to genuinely reproduce the actual reaction conditions in the industry this manipulation causes a well-known dilemma, because it brings the laboratory experiment further away from true industrial conditions, where the presence of adsorbed water is unavoidable: surface hydroxylation in industrially operating SCR catalysts is mainly due to water vapour from the combustion process and SCR-produced water is insignificant.

When NO and  $\text{NH}_3$  are brought in contact in dry SCR reaction conditions  $\text{H}_2\text{O}$  is formed, which induces a relative increase of the V-OH fraction, and thus converts  $\text{NH}_3$  to  $\text{NH}_4^+$ ; this can lead to the simplified conclusion that Brønsted acid sites are not consumed in the beginning of the experiment. This work demonstrates that MCR-ALS (Multivariate Curve Resolution Alternating Least Squares) allows differentiating the overlapping bands from adsorbed ammonia and adsorbed water, and therefore that FTIR characterization of surface ammonia species can be performed when water is present. The identification of the contributions from adsorbed water and ammonia species to the convoluted band by a model makes it possible to evaluate the interplay between Lewis and Brønsted acid sites on vanadia based catalysts, especially in a monolithic integral reactor, and opens up new possibilities for future *in-situ* and *operando* studies on their precise role in SCR under humid conditions. The use of MCR-ALS analysis in specially designed studies with ideal catalysts may get a deeper understanding on the different species that can be differentiated and followed by IR spectroscopy.

Monolithic reactors can sometimes be represented by a wafer or powder model catalysts. However, we have demonstrated that it is possible and advisable to investigate catalysts at work in their final form. In this *operando* FTIR-MS study on a whole V-W-TiO<sub>2</sub>-sepiolite monolith, with intact porosity and channel fluid dynamics, we have observed that in the  $\text{NH}_3$ -SCR reaction spatial effects along the monolith channel affect the gas-surface interface, represented by the interaction between surface sites, water, ammonia and ammonium ions. Although the spectra are less informative, we have achieved looking at the real system and not the idealized model.

The research using an integral monolithic reactor with NO and O<sub>2</sub> titrating the catalyst surface for pre-adsorbed ammonia demonstrates that a) water hydrolyzes molecularly dispersed vanadia species, creating new Brønsted acid sites, and b) adsorbed ammonia is either used for the SCR reaction, or converted into the ammonium ion, which then participates in the SCR reaction. These observations complement more fundamental works performed on kinetically restricted pelletized or powdered catalysts with valuable information on secondary effects from the water produced upstream.

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