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1 Modulated-Excitation Raman Spectroscopy of V₂O₅/TiO₂: Mechanistic
2 Insights into the Selective Catalytic Reduction of NO by NH₃

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ABSTRACT

We report the increased level of mechanistic information that Raman spectroscopy can provide when combined with modulated excitation experimentation. A V_2O_5/TiO_2 catalyst for the selective catalytic reduction (SCR) of NO_x was subjected to periodic NH_3 pulses while recording time-resolved Raman spectra simultaneously. Through phase sensitive detection, we confirmed unambiguously that both VO_x and TiO_2 play a dynamic role in the SCR process. Only a well-defined portion of VO_x species (i.e., those that are coordinatively unsaturated) act as catalytic active centers while the majority remain largely unresponsive. Although TiO_2 is not directly involved in the SCR reaction, the phase-resolved Raman spectra demonstrate that it acts as a reservoir of NH_3 molecules that can be mobilized to the active sites. The inherent depth of these molecular insights goes beyond what is currently achievable with Raman experiments under steady-state conditions. Modulated-excitation Raman spectroscopy can therefore advance the fundamental understanding of SCR and other metal oxide-catalyzed reactions.

Keywords: Mechanism; Modulated excitation; Operando spectroscopy; Raman spectroscopy; Selective catalytic reduction

1 INTRODUCTION

2 Selective catalytic reduction (SCR) is used to control NO_x emissions from chemical and power
3 plants and from diesel-powered vehicles. In this process, harmful NO_x is transformed into
4 benign N₂ in the presence of a selective reductant such as NH₃. The main reaction involved is
5 termed “standard SCR” and proceeds according to Equation 1.

7 V₂O₅/TiO₂-based catalysts have remained to be the most widely used for SCR since their
8 introduction in the 1970's. Their commercial success results from their high activity, good
9 resistance to sulfur poisoning, and moderate cost.¹ In this binary oxide system, V₂O₅ is present
10 as surface VO_x species and acts as the catalytic redox center while TiO₂ is the support, which
11 disperses the active phase and contributes to NH₃ adsorption.²

12 Several SCR reaction mechanisms have been proposed in the literature for V₂O₅/TiO₂.³⁻⁶
13 Despite the differences in the reported mechanisms, it is generally accepted that the reaction
14 proceeds via an integrated route composed of acid and redox cycles. In the first step, NH₃
15 coordinates with VO_x sites through an acid-base interaction. Adsorbed NH₃ then reacts with
16 NO, most probably from the gas phase, to form a nitrosamide intermediate. This step is also
17 accompanied by the reduction of the V center from a formal oxidation state of +5 to +4. The
18 formed intermediate then decomposes readily into N₂ and H₂O. In the last step, molecular O₂
19 reoxidizes the V center to the +5 state, releasing H₂O and closing the catalytic cycle.

20 Operando studies have advanced our view of the SCR reaction mechanism. For instance, IR
21 spectroscopy has been widely used to monitor the adsorption of reactants and formation of
22 intermediate species. In one of the pioneering IR studies, only NH₃ species were found to be
23 adsorbed on VO_x sites, suggesting that SCR proceeds through an Eley-Rideal mechanism.⁷
24 Further studies demonstrated that the V=O center is the active site of SCR and that while NH₄⁺
25 species were formed, their surface concentration did not actually correlate with catalytic

activity.⁸ More recently, our group verified the formation of the nitrosamide intermediate during the V reduction step in SCR using time-resolved IR spectroscopy.⁹ We further showed that NO reacts predominantly with NH₃ adsorbed on Lewis acid sites, noting that the depletion of Lewis-bound NH₃ was concomitant to the formation of the water by-product.

Whereas adsorbates are best probed by IR spectroscopy, changes within the metal oxide structure are preferentially monitored using Raman spectroscopy. Due to their highly polarizable bonds with predominantly covalent character, transition metal oxides such as V₂O₅ and TiO₂ give rise to intense Raman-active vibrational modes.¹⁰ In V₂O₅/TiO₂, vanadia is present exclusively as surface amorphous species at low loading, and microcrystalline domains appear only above the monolayer coverage.^{11,12} These surface vanadyl species are highly sensitive to the gas environment to which they are exposed.¹³ The presence of water and NH₃, for instance, can cause the V=O peak to redshift and attenuate, indicating molecular interaction.

Steady-state Raman experiments have undoubtedly revealed important structural information and redox features of the V₂O₅/TiO₂ system that cannot be obtained by other operando techniques. However, isolation of the structure of responsive species within the large contribution of stationary species still remains a challenge. In addition, TiO₂ is acknowledged to play a role in NH₃ adsorption during SCR¹⁴, but it has received only cursory attention in SCR mechanistic studies because the changes to its signals are subtle. These issues call for a new strategy for Raman studies because the conventional approach based on steady-state experimentation cannot advance our understanding of the reaction mechanism further. In an effort to extend the current capabilities of Raman spectroscopy, we performed experiments under transient conditions by applying the modulated excitation (ME) technique, wherein the concentration of one reactant is varied periodically while acquiring spectra of sufficient time resolution simultaneously.¹⁵ The collected spectra in the time domain are converted into the corresponding spectra in the phase domain,¹⁶ which contain the signals only from the species

that responded to the modulation sequence. Hence, signals from unresponsive or static species are effectively eliminated, and signals from the active sites and perturbed species are emphasized.^{9,16,17} Here we demonstrate the increased level of mechanistic details that can be derived from this approach compared to steady-state experiments in the Raman spectroscopy of V₂O₅/TiO₂.

RESULTS AND DISCUSSION

The time-resolved Raman spectra of the 2 wt% V₂O₅/TiO₂ catalyst (Figure 1a) are dominated by the contribution from the anatase phase of TiO₂.¹⁸ The intense peaks at 395 and 636 cm⁻¹ correspond to the B_{1g} and E_g modes, respectively, and the peak at 516 cm⁻¹ is a convolution of the two Raman-active modes B_{1g} and A_{2g}.¹⁹ The weak band at around 800 cm⁻¹ is the second overtone of the B_{1g} mode. The most prominent feature of the VO_x species is the weak peak in the region of 1010-1040 cm⁻¹ which is readily assigned to the ν(V=O) stretch mode.¹¹⁻¹³ The submonolayer coverage of 2 VO_x·nm⁻² was confirmed by the absence of the bulk V₂O₅ peak at 995 cm⁻¹ and by the X-ray diffraction data (Figure S1).²⁰ Therefore, all the vanadyl species occurred exclusively as amorphous VO_x on the surface of TiO₂. The catalyst loading was kept low at 2 wt% to be as close to the formulation of real-life industrial catalysts.

Figure 1. (a and b) Time-resolved Raman spectra and (c and d) the corresponding phase-resolved spectra of 2 wt% $\text{V}_2\text{O}_5/\text{TiO}_2$ at 250 °C during 30-s pulses of 500 ppm NH_3 in a gas feed of 500 ppm NO, 2 vol% H_2O , and 5 vol% O_2 balanced in Ar.

For the purpose of the ME experiments, the SCR reaction was repeatedly switched on and off by pulsing NH_3 in a gas feed containing NO (Figure S2). The experiment was performed at 250 °C where the NO conversion was 26% (Figure S3). Under these conditions, the surface of the catalyst was populated by adsorbed water and NH_3 (Figure S4).

No spectral changes are immediately noticeable in the time-resolved Raman spectra (Figure 1a), but it is clear after phase sensitive detection (PSD) that the signals of both VO_x and TiO_2 responded to the changes in the gas phase composition (Figure 1c). Control ME experiments in the absence of SCR activity performed by (1) replacing the SCR reactants with Ar pulses on $\text{V}_2\text{O}_5/\text{TiO}_2$ at 250 °C, (2) applying NH_3 pulses in NO on $\text{V}_2\text{O}_5/\text{TiO}_2$ at room temperature, and (3) applying NH_3 pulses in NO on TiO_2 at 250 °C provided negligible phase-resolved signal

(Figure S5). Hence, the first information from the ME Raman data shown in Figure 1 is that both the VO_x active phase and the TiO_2 support are involved in the SCR process to some extent. It is apparent in Figure 1b that the $\nu(\text{V}=\text{O})$ mode is very broad the time-resolved spectra, but it is present as a narrower and well-defined peak in the phase-resolved spectra (Figure 1d). This suggests that while some of the VO_x species were perturbed by the NH_3 pulses and thus provided the phase-resolved signal, most of the VO_x population remained largely unresponsive. Therefore, only a defined portion of VO_x species participate in the SCR reaction.

To interpret Figure 1 further, we determined the influence of each individual gas component on the Raman spectra. Changes in the shape, intensity, and energy of Raman bands reflect structural transformations within the catalyst. A simplified model such as the ball-and-spring model can help to rationalize these phenomena as they relate to molecular vibrations.^{21,22} In the context of the present experiment, a change in force constant (κ) occurs when the bond order increases/decreases while a change in reduced mass (μ) takes place when substrate molecules adsorb/desorb. Figure 2 displays the evolution of the $\nu(\text{V}=\text{O})$ mode upon exposure of $\text{V}_2\text{O}_5/\text{TiO}_2$ to SCR-relevant gases. Under O_2 , the peak appeared relatively narrow and centered at 1031 cm^{-1} . The species responsible for this signal correspond to vanadyl Lewis acid sites. Upon water introduction, the peak broadened considerably and redshifted to 1026 cm^{-1} . Water can act as a Lewis base and adsorb on the VO_x sites or form a network of hydrogen bonds with the oxidic structure of the catalyst surface.^{11,13} In both cases, μ increases which translates into a redshift. It is also able to hydroxylate some of the $\text{V}=\text{O}$ bonds, transforming them from Lewis to Brønsted-Lowry acid sites. NH_3 , a much stronger base, produced an even more pronounced effect. The initial $\text{V}=\text{O}$ peak was barely discernable and shifted even further to 1016 cm^{-1} . NH_3 may interact with the catalyst in at least two ways. Firstly, it can adsorb on vacant Brønsted-Lowry and Lewis sites of VO_x , and on the Lewis Ti^{4+} sites of the support (Figure S6).^{9,23} These molecular events change μ due to the additional mass of strongly bound NH_3 . Secondly, NH_3

can reduce the vanadyl center and change the bonding of V with the O atoms, thus affecting κ . The peak shifts indicate that NH_3 interacts more strongly with VO_x than water, which is in agreement with previous reports and the corresponding IR spectra under these conditions (Figure S7).^{7,13}

Figure 2. Raman spectra of 2 wt% $\text{V}_2\text{O}_5/\text{TiO}_2$ at 250 °C showing the changes of the V=O peak under different gas environments: 5 vol% O_2 balanced in Ar (black); 2 vol% H_2O and 5 vol% O_2 balanced in Ar (blue); 500 ppm NH_3 , 2 vol% H_2O , and 5 vol% O_2 balanced in Ar (green).

TiO_2 responded to the changes in the gas environment as well (Figure S8). The intensity of the characteristic TiO_2 peaks decreased slightly upon exposure to water and NH_3 , but they retained their energy positions. This suggests that there is a marked difference between the scattering power of “free” TiO_2 and adsorbate-bound TiO_2 . The subtle response of TiO_2 is a direct consequence of its role as the catalyst support. While VO_x is well-dispersed and occurs exclusively on the surface, TiO_2 also exhibits bulk domains. In contrast to the surface species that can accommodate adsorbates, the great majority of Ti-O bonds providing the Raman signal is in the bulk and cannot interact with the molecules in the gas phase. Hence, the overall change

of the Raman intensity is not large because only a small fraction of TiO_2 (i.e., the surface atoms) is probed by the changes in the gas feed.

We now expand our discussion of the ME Raman data in light of the steady-state experiments.

Figure 1b,d shows that the $\nu(\text{V}=\text{O})$ mode does not coincide in the time-resolved and phase-resolved domains. In the former, it is centered at around $1016\text{--}1026\text{ cm}^{-1}$ which is expected due to the presence of water and NH_3 (Figure 2). In the phase-resolved spectra, however, the maximum occurs at 1031 cm^{-1} , which is reminiscent of the VO_x species observed in the absence of adsorbates. Therefore, the responsive VO_x species are most likely coordinatively unsaturated. From a mechanistic perspective, this is intuitive since the active site cannot be coordinated to another molecule in order to accommodate the reactant with which it will perform the catalysis. While the majority of the VO_x population is engaged with adsorbed/coordinated molecules of water and NH_3 as indicated by the time-resolved data (Figure 1b), the portion of VO_x – which becomes coordinatively unsaturated during the pulse sequence – is able to perform the redox cycle of the SCR reaction. The practical relevance of this molecular level information is demonstrated by the finding that the presence of hydroxylation-resistant species positively correlated with the increased NO reduction rates of activated catalysts.²⁴

A weak peak was also observed at 1022 cm^{-1} in the phase-resolved spectra which appears to vary asynchronously with the main $\nu(\text{V}=\text{O})$ mode (Figure 1d). Our steady-state experiments shown in Figure 2 suggests that this peak is not associated with a coordinatively unsaturated species because it is significantly redshifted from the dehydrated VO_x peak at 1031 cm^{-1} ; rather, this VO_x species appears to be bound to a ligand, particularly NH_3 which induces the VO_x peak maximum to shift. In light of these observations, we tentatively assign this peak to the VO_x species that were previously bound to NH_3 . As soon as the products are desorbed from the catalyst surface, the coordinatively unsaturated VO_x species are formed again. The transition

from the NH_3 -coordinated (1031 cm^{-1}) to the coordinatively unsaturated state (1022 cm^{-1}) as soon as the reaction occurs can explain the phase lag between the two peaks.

To isolate the effect of reaction from adsorption/desorption, we performed NH_3 pulsing experiments in the absence of NO (Figure 3). As in the previous case, changes around the $\nu(\text{V}=\text{O})$ mode during NH_3 pulses without NO became very noticeable only in the phase-resolved spectra (Figure 3b). In contrast to the behavior under SCR conditions, the response of TiO_2 to NH_3 adsorption-desorption was very limited. Instead, it was the signal of VO_x that exhibited the greatest intensity variation.

Figure 3. (a and b) Time-resolved Raman spectra and (c and d) the corresponding phase-resolved spectra of 2 wt% $\text{V}_2\text{O}_5/\text{TiO}_2$ at $250\text{ }^\circ\text{C}$ during 30-s pulses of 500 ppm NH_3 in a gas feed of 2 vol% H_2O and 5 vol% O_2 balanced in Ar.

Molecular NH_3 can adsorb on either the V^{5+} sites of VO_x or the Ti^{4+} sites of TiO_2 . Previous studies have demonstrated that NH_3 is more strongly (and will be preferentially) adsorbed on the Ti^{4+} sites especially at low V loading.¹³ The ME results are consistent with this behavior

1 since the signal from TiO₂ is practically absent in the phase-resolved spectra. During the first
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1 since the signal from TiO₂ is practically absent in the phase-resolved spectra. During the first
2 few pulses of NH₃, all of the TiO₂ sites on the surface might have already been saturated with
3 NH₃ molecules which are so strongly bound that they do not desorb significantly even in the
4 presence of water at 250 °C. This stable interaction renders TiO₂ only weakly responsive to the
5 perturbations in the gas environment, as supported by the IR spectra (Figure S6b). In contrast,
6 the interaction of NH₃ with VO_x sites is much weaker. At 250 °C, some adsorbed NH₃ species
7 – particularly those at Brønsted-Lowry sites – may desorb due to poor thermal stability (Figure
8 S6a).²⁵ When NH₃ is present in the feed, it can adsorb on the VO_x sites; once the NH₃ supply
9 is interrupted, NH₃ can desorb from those sites where the adsorption is rather weak. The
10 liberated sites can then be occupied by new NH₃ molecules when the supply is turned on again.
11 This dynamic behavior explains the significant presence of the V=O peak in the phase-resolved
12 spectra.
13 Under steady-state conditions, the presence of NH₃ caused the V=O peak to shift from 1031 to
14 1016 cm⁻¹ (Figure 2). In the NH₃ adsorption ME experiment, the maximum of the V=O signal
15 in the phase-resolved spectra was centered at 1025 cm⁻¹ (Figure 3d), which corresponds to the
16 observed redshift when water is present in the steady state spectra. Hence, it seems that the
17 responsive VO_x species during NH₃ adsorption/desorption are coordinatively saturated and
18 bound to ligands. This process is different from the one discussed in Figure 1.
19 The same ME experiment was repeated by pulsing NO, the other key reactant in standard SCR
20 (Figure S9). The phase-resolved spectra did not deliver any discernable signal, indicating that
21 neither VO_x nor TiO₂ was perturbed significantly by the NO pulses. This result is consistent
22 with the generally accepted view that NO is not strongly adsorbed on the V₂O₅/TiO₂ surface.⁷
23 Unlike NH₃, NO is not basic and cannot interact with the acidic sites of the catalyst.
24 It is remarkable to note that TiO₂ peaks are present in the PSD data when NH₃ was pulsed in a
25 gas feed containing NO (Figure 1) whereas they are almost nonexistent if NO was absent

(Figure 3). This confirms that TiO_2 plays a dynamic role in the SCR process; it also discards the possibility that the phase-resolved signals observed in Figure 1 and Figure 3 are provoked solely by color changes due to the redox VO_x species, which could also result in intensity changes. Furthermore, when TiO_2 alone was subjected to the same pulsing sequences, no significant spectral changes were observed (Figure S5e). When there was no SCR reaction, most of the adsorbed NH_3 molecules remained bound to TiO_2 even in the presence of water at 250 °C, which was confirmed by equivalent IR experiments (Figure S6b). However, when the feed returned to SCR conditions, TiO_2 -bound NH_3 molecules were mobilized to the VO_x active sites to react with NO. Although TiO_2 is not directly involved in the actual SCR reaction at this temperature, this NH_3 storage and release mechanism rationalizes the presence of the characteristic Raman peaks of TiO_2 in the phase-resolved spectra. We therefore provide evidence using ME Raman spectroscopy that TiO_2 acts as a dynamic pool of adsorbed NH_3 . The role of TiO_2 is further exemplified by the differences in the behavior of the responsive species in the phase-resolved spectra. In Figure 1c, both VO_x and TiO_2 vary in-phase because under SCR conditions, the delivery of NH_3 from TiO_2 to VO_x is frequent. In contrast, VO_x and TiO_2 vary out-of-phase in Figure 3c because NH_3 adsorption/desorption require no delivery of NH_3 to the active sites.

We then consider the relationship between phase angle and time domain.²⁶ Figure 4 shows the evolution of the normalized signal intensity of TiO_2 and VO_x appearing in Figure 1c as a function of phase angle. The phase angle dependence of the characteristic peaks of TiO_2 at 395 and 515 cm^{-1} was identical. This is justified by the fact that while these two peaks originate from different symmetry representations, they both stem from the same molecular species. On the contrary, the peak at 1031 cm^{-1} , which corresponds to VO_x groups, was shifted by approximately 9° with respect to the TiO_2 peaks. The phase delay between VO_x and TiO_2 suggests that the two species followed non-identical behaviors during the NH_3 pulse, and that

coordinatively unsaturated VO_x species appeared prior to liberation of adsorbed NH_3 from TiO_2 . Given the high level of noise in the time-resolved spectra, such type of kinetic information can be obtained solely from the phase-resolved spectra.

Figure 4. Phase angle dependence of the Raman signal intensity of $\text{V}=\text{O}$ and TiO_2 during SCR on/off experiments.

The maximum intensity variation of the VO_x signal in the phase-resolved spectra correlated with the SCR activity (Figure 5). As NO conversion decreased with decreasing temperature, the peak intensities of VO_x and TiO_2 decreased as well. In the phase domain, the signal intensity depends on the fraction of dynamic species perturbed by the repeated gas pulses. The interaction strength between the molecular adsorbates and the metal oxides increases with decreasing temperature, and hampers molecular motion and desorption. Furthermore, fewer NH_3 molecules are activated at the VO_x sites at lower temperature and correspondingly, less NH_3 molecules need to be transferred from TiO_2 . The decrease in the SCR activity reduced the fraction of dynamic species involved, which in turn resulted in less intense signals in the phase-resolved spectra.

Figure 5. Effect of temperature on the (a) in-phase phase-resolved spectra and (b) their VO_x region. Conversion values: 25°C, 0%; 150°C, 4%; 200°C, 10%; 250°C, 26%.

The activity decrease was accompanied by the redshift of the VO_x peak maximum from 1031 to 1029 cm⁻¹, which may be associated to the increase in the population of hydrated VO_x species. As the temperature decreased, water desorption from the catalyst was increasingly less favorable. The relatively narrow shape of the VO_x peak was retained, but the peak area decreased with decreasing temperature. This suggests that even a smaller fraction of the VO_x species were active for SCR at low temperatures, which is supported by the activity measurements (Figure S3). Even at a conversion level of 4%, changes were observed in the phase-resolved spectra. In contrast, the time-resolved spectra at 26% conversion (Figure 1a) did not provide any discernable change. This demonstrates the sensitivity enhancement that PSD offers to Raman spectroscopy.

Arrhenius-type relationships confirmed the involvement in SCR of the coordinatively unsaturated species to SCR giving rise to the phase-resolved signal at 1031 cm⁻¹. Figure 6 shows that the maximum peak intensity of these species in the phase-resolved data correlates with the rate constant (*k*) under steady-state. An apparent activation energy of around 40 kJ·mol⁻¹ is comparable to those obtained for V₂O₅/TiO₂ catalysts.²⁷

Figure 6. Arrhenius plots constructed from $\ln(k)$ (○) and VO_x Raman peak intensity (■).

CONCLUSIONS AND OUTLOOK

In summary, the application of ME and PSD revealed important mechanistic information about SCR that are not apparent in steady-state Raman experiments. We have provided mechanistic evidence using the ME approach that (1) both the VO_x active phase and the TiO_2 support are involved in the SCR process; (2) only a defined portion of the VO_x species are active in the SCR reaction, and they are coordinatively unsaturated; and (3) TiO_2 acts as a reservoir of NH_3 molecules which can be delivered to the VO_x sites to react if NO is present. These novel mechanistic insights could be extracted from the Raman spectra only due to the increased sensitivity offered by ME experimentation and PSD.

Further ME Raman studies on V_2O_5 -based catalysts should focus on the effect of promoters and of gas phase components such as NO_2 and SO_2 , which co-exist with the standard SCR

1 reactants in the exhaust gas. The presence of NO₂ shifts the catalytic system towards the *fast*
2 SCR reaction, whose mechanism can also be investigated using our approach.
3 To achieve the required time resolution, we have used an IR laser source for our experiments.
4 UV laser sources are expected to deliver even more structural information due to resonance
5 scattering effects,²⁸ but they are currently limited by their long acquisition times. Hence, future
6 improvements in UV Raman spectroscopy will certainly benefit the ME approach.
7 In this study, we have demonstrated the utility of ME Raman spectroscopy in the specific case
8 of SCR, but the technique can be easily adapted to study the mechanism of other industrially
9 relevant reactions, especially those that are catalyzed by metal oxides. Therefore, ME Raman
10 spectroscopy opens up new possibilities in deciphering structure-reactivity relationships of
11 metal oxide catalyst systems using Raman spectroscopy.

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17 18 **SUPPORTING INFORMATION**

19 Experimental part including catalysts synthesis, catalyst characterization, determination of
20 catalytic activity, Raman and DRIFT spectroscopy; phase sensitive detection; XRD data;
21 concentration of reactants/products from mass spectrometer; catalytic activity of catalyst;
22 DRIFT spectra under various experimental conditions; Raman spectra of control experiments;
23 and laser damage test.

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