An Application of Steady-state Isotopic-transient Kinetic Analysis (SSITKA) in DeNO\textsubscript{x} Process

Magdalena Jabłońska\textsuperscript{[a]}

[Diagram and text related to the DeNO\textsubscript{x} process and SSITKA analysis]

\textsuperscript{[a]} Department of Chemistry, Faculty of Chemistry, University of Warsaw, ul. Pasteura 1, 02-093 Warszawa, Poland.

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This Minireview presents an overview of the advancement and capabilities of the steady-state isotopic transient kinetic analysis in the selective catalytic reduction of NO₂. Firstly, a brief overview of the method and the kinetic parameters of catalyst-surface reaction intermediates, including concentration and coverage of surface intermediates, surface residence time and intrinsic turnover frequency (TOF), is provided. Furthermore, the focus is on the application of SSITKA or a unique combination of SSITKA-DRIFTS for the identification of active and/or inactive (spectators) species in NH₃-SCR, H₂-SCR and HCs-SCR. Different forms of adsorbed species and their formation rates revealing the main elementary steps on the catalyst’s surface involving labeled molecules are discussed. The emphasis is laid on the optimization and design of industrial catalysts.

1. Introduction

Steady-state isotopic transient kinetic analysis (SSITKA) was developed in large part by Biloen,[1] Bennett,[2] Happel[3] and Bell[4] and is applied in the heterogeneous catalysis for the understanding of the reaction pathway of surface-catalyzed reactions. Extensive details (i.e., a typical system for isotopic transient kinetic study, SSITKA modeling, limitations and corrective techniques, advanced mathematical analysis and applications in different chemical reactions) about SSITKA (for measurements under adsorption/desorption reaction equilibrium) or ITKA (for measurements that are not at steady state) are given in references.[5–8] The technique consists of allowing the reaction to reach steady-state using an unlabeled reaction mixture and abruptly switching from the unlabeled mixture to the labeled one (without perturbation of the steady-state catalytic process). Consequently, the total rate of formation of any product (i.e., the chemical composition of the surface) does not change due to the abrupt replacement of one reactant by its isotope. The accurate in situ determination of kinetic parameters, such as surface residence time \( \tau_p \), concentration \( N_p \) and coverage \( \theta_p \) of the main intermediates (not of any inactive (spectator) species) or their turnover frequency \( \text{TOF}_{\text{ITT}} \) by SSITKA allows to determine the reaction mechanism.

For a given reversible heterogeneous catalytic reaction at steady-state, a constant amount of reactant \( R \) is transformed into a product \( P \) through an adsorbed intermediate \( X \) (Eq. (1)):

\[
R(g) + \text{other reactants}(g) \leftrightarrow X(\text{ads}) \rightarrow P(g) + \text{other products}(g)
\]  

(1)

By continuously monitoring the relaxation and evolution of the unlabeled and labeled species via mass spectrometry (with high resolution), isotopic transient curves can be obtained. Figure 1 shows typical normalized isotopic-transient responses of a species \( F(t) \) as a function of time after the isotope switch.[9]

The surface residence time \( \tau_p \), of the intermediates leading to product is determined from the area between inert tracer \( \text{Ar} \) or \( \text{Kr} \) that does not adsorb on the catalysts’ surface, \( F_0 \) and product \( F_v \) transient response curves [Eq. (2)][5]

\[
\tau_p = \int_0^\infty F_v(t) dt - \int_0^\infty F_0(t) dt = \int_0^\infty (1 - F_0/v)(t) dt 
\]  

(2)

Based on the surface residence time \( \tau_p \), and the formation rate of the unlabeled product \( \mu_p \), the concentration of the most active surface intermediates \( N_p \), \( \mu_p \), can be determined [Eq. (3)]:

\[
N_p = \tau_p \cdot \rho_p = \frac{F \cdot X}{W}
\]  

(3)

where \( F \) – molar flow rate of gas, \( \mu_p \), \( \mu_p \) – conversion to the product, \( W \) – catalyst's weight, \( g \).[6] Furthermore, the surface coverage \( \theta_p \) is calculated based on the number of adsorbed species \( N_p \) and the total number of the active sites \( N_t \) mainly determined by \( H_2 \) chemisorption [Eq. (4)]:

\[
\theta_p = \frac{N_p}{N_t}
\]  

(4)

The turnover frequency on the average site participating in product formation \( \text{TOF}_{\text{ITT}} \), can be estimated by taking the reciprocal of \( \tau_p \) [Eq. (5)]:

\[
\text{TOF}_{\text{ITT}} = \frac{\tau_p}{N_t}
\]  

(5)

The values of \( \text{TOF}_{\text{ITT}} \) are higher than \( \text{TOF}_{\text{SS}} \) (turnover frequency based on the concentration of true active sites) and...
also $TOF_{\text{Chem}}$ (turnover frequency based on chemisorption), and follows the relationship: $TOF_{\text{Tot}} \geq TOF_{\text{sys}} \geq TOF_{\text{Chem}}$. Thus, SSITKA allows us to determine the number of active centers on the working catalyst. SSITKA provides on the homogeneity or heterogeneity of the catalyst’s surface and insight into the possible mechanism. The simplest way is to analyze the shape of the curves showing the change in product concentration as a function of time that has elapsed since switching between reactants with different isotope composition. E.g., Figure 2 presents the transient responses for an irreversible-reaction mechanism consisting of a single pool, two serial pools or two parallel pools.

Different applications - in ammonia synthesis, CO hydrogenation (methanation and Fischer-Tropsch synthesis), methane activation (coupling, partial/tot oxidation), methane reforming, water-gas-shift (WGS), selective catalytic reduction of NO$_x$ (discussed below) and many other catalytic processes, have demonstrated the versatility of the SSITKA technique. Effects of temperature, reactant partial pressure and metal promotions on the catalysts or cause of deactivation (e.g., [15,20,21]) have also been explored using SSITKA. It has been shown that in many cases there is an increase of active surface intermediates rather than the increase of intrinsic activity. Thus, a better understanding of reaction at the site level is provided, resulting in better catalyst design. SSITKA experiments on DeNO$_x$ reactions have been published for example in NH$_3$–SCR over V$_2$O$_5$/TiO$_2$ [22–24] CH$_x$–SCR over Pt/TiO$_2$ [25] La$_2$O$_3$–CaO [26] or Co/ZSM-S [27,28] CH$_x$–SCR over Pt/SiO$_2$ [29,30] and H$_2$–SCR over Pt/SiO$_2$ [31,32] Pt/La–Ce–Mn–O [33] and Pt/SiO$_2$ [33,34] etc. (Table 1).

2. Selective NO Reduction

Nitrogen oxides (NO, NO$_2$ and N$_2$O) released from both mobile and stationary sources are considered major air pollutants that contribute considerably to the formation of photochemical smog, acid rain, ozone depletion, ground-level ozone and greenhouse effect, etc. The selective catalytic reduction with NH$_3$ (NH$_3$–SCR) is the currently commercialized aftertreatment system for NO removal in coal-fired power plants and diesel engine vehicles. However, many problems are encountered in the use of NH$_3$–SCR technology, namely catalysts deterioration, NH$_3$-slip (emission of unreacted toxic NH$_3$), ash odor, air heaters fouling and high running cost. Thus, SCR of NO with H$_2$ or hydrocarbons (HCs–SCR, CH$_x$–SCR or C$_x$H$_y$–SCR) has been considered as an alternative technology. In the literature, the application of SSTKTA or its combination with diffuse reflectance infrared Fourier transform spectroscopy (SSITKA–DRIFTS) studies focus mainly on NO reduction by CH$_4$ or H$_2$, which are presented in the following sections.

2.1. NO reduction by NH$_3$ and NH$_3$ oxidation

The selective catalytic reduction of NO with NH$_3$ under strongly oxidizing conditions (NH$_3$–SCR) was first introduced in the early 1970s by Hitachi Zosen in Japan over V$_2$O$_5$/TiO$_2$ [35,36]. Currently, the investigated catalysts in NH$_3$–SCR can be divided into three categories: noble metal-based catalysts (e.g., Ag/Al$_2$O$_3$), transition metal oxides (e.g., Cu(Fe)-Mg–Al, Mn/Ti-SiO$_2$) and transition metal ion-exchanged zeolites (e.g., Cu(Fe)-ZSM-5, CuSSZ-13). The studies can be found in numerous review articles. The SSITKA studies over selective catalytic NO reduction by NH$_3$ (NH$_3$–SCR) or selective catalytic NH$_3$ oxidation to N$_2$ (NH$_3$–SCO) are rather rare, e.g., Otto et al. [39] in his early studies in 1970, investigated the interaction of NO with NH$_3$ (without O$_2$) over (0.81 wt.%)Pt/Al$_2$O$_3$ at 200–250 °C. Overall, based on the SSITKA experiments and by applying mainly labeled NH$_3$ (poss. 1, Table 1), they found that N$_2$ (and N$_2$O in minor part) is formed predominantly from the interaction of one molecule of NH$_3$ and NO [Eqs. (6–7)]. Furthermore, N$_2$ and N$_2$O can be formed by the interaction of a pair of NO molecules with chemisorbed hydrogen (from dissociative chemisorption of NH$_3$ [Eqs. (6–9)]).

\[
\text{NO} + 15\text{NH}_3 \rightarrow N_2^\text{ads} + H_2O + (H)_{\text{ads}} \quad (6)
\]

\[
\text{NO} + 15\text{NH}_3 \rightarrow 15\text{NNO} + 3(H)_{\text{ads}} \quad (7)
\]

\[
2\text{NO} + 2(H)_{\text{ads}} \rightarrow N_2 + H_2O \quad (8)
\]

\[
2\text{NO} + 4(H)_{\text{ads}} \rightarrow N_2 + 2H_2O \quad (9)
\]
Table 1. Examples of the studies carried out for the selective catalytic reduction of NO employing SSITKA.

| Pos. | Catalyst | Isotopic experiments | Main conclusions | Ref. |
|------|-----------|----------------------|------------------|------|
| 1    | (0.81 wt.%)Pt/Al₂O₃ | NO reduction by NH₃ and NH₃ oxidation | 1) NH₃/NO/Ar→NH₃/NO/Ar 60–120 Torr NO, 30–60 Torr NH₃, 300 Torr Ar, 200°C exchange of gaseous O₂ with catalyst’s lattice oxygen | [21] |
| 2    | V₂O₅/TiO₂ (1.9 wt.% of V) | 1) NH₃/NO/O₂/He→NH₃/NO/O₂/He 0.05 Vol.% NO, 0.05 Vol.% NH₃, 0.0455–0.0581 Vol.% O₂, He balance, 400°C | N₂ and/or NO₂ formed from one molecule of NH₃ and one molecule of NO V=O as active sites for NH₃ activation | [22] |
| 3    | V₂O₅/TiO₂ | NO reduction by NH₃ and NH₃ oxidation | 1) NH₃/NO/O₂/He→NH₃/NO/O₂/He 0.05 Vol.% NO, 0.473–0.05 Vol.% NH₃, 0.0455–0.0581 Vol.% O₂, He balance, 400°C | [23] |
| 4    | V₂O₅ (preferential exposure of the side planes) | NO reduction by NH₃ and NH₃ oxidation | 1) NH₃/O₂/He→-¹¹²⁵⁷O²/He 0.15 Vol.% NO, 0.15 Vol.% NH₃, 0.15 Vol.% O₂, He balance, 400°C | [24] |
| 5    | (3.6, 9.0 wt.) V₂O₅/TiO₂ | NO reduction by NH₃ and NH₃ oxidation | 1) NH₃/O₂/He→NH₃/O₂/He 0.15 Vol.% NH₃, 1 Vol.% O₂, He balance, 350°C | [25] |
| 6    | (9.0 wt.) V₂O₅/TiO₂ | NO reduction by NH₃ and NH₃ oxidation | 1) NO/O₂/He→O/O₂/He 1 Vol.% NO, He balance, 400°C | [26] |
| 7    | (2.0 wt.%Mn/Al₂O₃ | NO reduction by NH₃ and NH₃ oxidation | 1) NH₃/NO/O₂/He→NH₃/NO/O₂/He 0.05 Vol.% NO, 0.05 Vol.% NH₃, 2 Vol.% O₂, He balance, 150°C | [27] |
| 8    | (5.0 wt.%Pt/SiO₂ | NO reduction by H₂ | 1) NO/H₂/O₂/He→NO/H₂/O₂/He 1.64 Vol.% NO, 1.64 Vol.% H₂, 8.7 Vol.% O₂, He balance, 60 and 83°C limited exchange of gaseous O₂ with catalyst’s lattice oxygen | [28] |
| 9    | (1.0 wt.%Pt/Al₂O₃ | NO reduction by H₂ | 1) NO/H₂/O₂/He→NO/H₂/O₂/He 0.76 Vol.% NO, 1.08 Vol.% H₂, He balance, 55–80°C | [29] |
| 10   | (1.0 wt.%Pt/SiO₂ | NO reduction by H₂ | 1) NO/H₂/O₂/He→NO/H₂/O₂/He 0.76 Vol.% NO, 1.08 Vol.% H₂, He balance, 55–80°C limited exchange of gaseous O₂ with catalyst’s lattice oxygen | [30] |
| 11   | (0.1 wt.%Pt/SiO₂ | NO reduction by H₂ | 1) NO/H₂/Ar→NO/H₂/Ar 1 Vol.% NO, 1 Vol.% H₂, He balance, 140°C chemical structure of NO, adsorbed precursor intermediate species depends on the catalysts composition and applied reaction temperature | [31] |
| 12   | (0.1 wt.%Pt/MgO-Ce₂O₃ | NO reduction by H₂ | 1) NO/H₂/Ar→NO/H₂/Ar 0.25 Vol.% NO, 1 Vol.% H₂, 5 Vol.% O₂, He balance, 140°C | [32] |
| 13   | (0.1 wt.%Pt/MgO-Ce₂O₃ | NO reduction by H₂ | 1) NO/H₂/Ar→NO/H₂/Ar 0.25 Vol.% NO, 1 Vol.% H₂, 5 Vol.% O₂, He balance, 140°C | [33] |
| 14   | (0.1 wt.%Pt/Ce₂Zr₃O₇ | NO reduction by H₂ | 1) NO/H₂/Ar→NO/H₂/Ar 0.05 Vol.% NO, 0.8 Vol.% H₂, 5 Vol.% O₂, He balance, 140°C | [34] |
| 15   | (2.0 wt.%Pd/TiO₂ | NO reduction by H₂ | 1) NO/H₂/Ar→NO/H₂/Ar 0.25 Vol.% NO, 1 Vol.% H₂, 5 Vol.% O₂, He balance, 140°C | [35] |

N₂ formed through direct participation of CH₄ and N₂O formed through NO decomposition | [36] |
The formation of (unmixed) N$_2$ was more pronounced over CuO than Pt/Al$_2$O$_3$. They excluded the reaction between two NH$_3$ molecules due to the absence of $^{15}$N$_2$ and/or $^{15}$N$_2$. Janssen et al.$^{[25]}$ claimed that oxidation of $^{15}$NH$_3$ to $^{15}$N$_2$ takes place in the absence of NO (at 400 °C). However, as they also mentioned $^{16}$N$_2$ (m/e 30) coincides with the mass of NO, which can also be formed during NH$_3$ oxidation. Otherwise, there was no mention of NO and/or N$_2$O formation in their study. In NH$_3$-SCR, N$_2$ and/or N$_2$O arise form one molecule of NO and one molecule of NH$_3$ (cross-labeled N$^{15}$N and N$^{13}$NO) over V$_2$O$_5$, V$_2$O$_5$/TiO$_2$, V$_2$O$_5$/SiO$_2$/Al$_2$O$_3$ and V$_2$O$_5$/Al$_2$O$_3$ (1.9–58 wt.% of V). The V=O species serve as active sites for NH$_3$ activation. The lattice oxygen of the catalyst participates in NH$_3$-SCR ($^{15}$NH$_3$+NO$^{18}$O$\rightarrow$NH$_3$+NO$^{18}$O$+^{16}$O$_2$ and vice versa) and is exchanged during the reaction (at 300–400 °C) with gaseous $^{18}$O$_2$. The formation of N$^{15}$O was attributed exclusively to the scrambling of NO with V=O groups.$^{[130]}$ Overall, the authors analyzed mainly isotope transfer with time without a detailed analysis of experimental data. Kinetic parameters as the surface residence time and the surface concentration of reaction intermediates were not fully explored in such studies.

Ozkan et al.$^{[135]}$ investigated the NH$_3$+$^{15}$NO$+^{18}$O$\rightarrow$NH$_3$+$^{15}$NO$+^{18}$O$+^{16}$O$_2$ or NH$_3$+$^{15}$NO$^{18}$O$+^{16}$O$_2$ → NH$_3$+ $^{15}$NO$+^{16}$O$+^{18}$O$_2$, switch over unsupported V$_2$O$_5$ and reported that the lack of doubly labeled N-species ruled out the possible formation of N$_2$ and/or N$_2$O through NO-NO interaction. The doubly unlabeled species (N$_2$ and/or N$_2$O) were assigned as NH$_3$ oxidation products, whereas cross-labeled species (N$^{15}$N and N$^{15}$NO) result form NO + NH$_3$ interaction. Otherwise, the unlabeled and cross-labeled NO is formed as a result of direct NH$_3$ oxidation. Furthermore, $^{15}$NO results from oxygen exchange between $^{15}$N$^{18}$O molecules and the catalyst's lattice as well as NH$_3$ oxidation using lattice oxygen. The authors claimed the existence of more than one type of adsorbed NH$_3$ species on V$_2$O$_5$ surfaces, i.e., namely V-ONH$_2^\delta$, V-ONH$_1^\delta$, and V-ONH$_2$ and pointed out sites responsible for NH$_3$ oxidation to NO and sites responsible for NH$_3$-SCR. The V-ONH$_2$ species were believed to be promoted to NO [Eq. (10)]:

$$\text{NO} + \text{H}_2\text{C}=\text{H}_2 \xrightarrow{\text{V}-\text{ONH}_2^\delta} \text{NO} + \text{H}_2\text{C}=\text{H}_2$$

[10]

The V-ONH$_2$ species lead to the formation of N$_2$ and/or N$_2$O [Eqs. (11–13)]

$$\text{V-ONH}_2^\delta + \text{O} \xrightarrow{\text{s}} 2 \text{N}_2\text{O}_3 + \text{H}_2\text{O} + \text{N}_2$$

[11]

$$\text{V-ONH}_1^\delta + \text{O} \xrightarrow{\text{s}} 2 \text{N}_2\text{O}_3 + \text{H}_2\text{O} + \text{N}_2$$

[12]

Table 1. continued

| Pos. | Catalyst | Isotopic experiments | Main conclusions | Ref. |
|------|----------|----------------------|------------------|------|
| 16   | (1.8 wt.%)Co/ZSM-5 | 4) $^{15}$CH$_2$/He→NO/He | CH$_3$–SCR proceeds with the participation mainly of NO$_{2-4}$ and NO$_2^-$ species | [27,28,4,46] |
|      |          | 5) $^{15}$CH$_2$/NO(O)/He→NO/He | different location of NO adsorbed precursor intermediate species | |
|      |          | 6) $^{15}$CH$_2$/He→O$_2$/He |        | |
|      |          | 7) CH$_2$/NO/O$_2$/He→CH$_3$/N$^{15}$O/O$_2$/He |        | |
|      |          | 0.15% NH$_3$, 0.89 Vol.% O$_2$, He balance, 500 °C |        | |
|      |          | 1) $^{15}$N$^{15}$O/He→$^{15}$N$^{15}$O/He | 0.6 or 1.2 Vol.% NO, He balance, 450 °C | |
|      |          | 2) $^{15}$N$^{15}$O/O$_2$/He→$^{15}$N$^{15}$O/O$_2$/He | 0.6–1.2 Vol.% NO, 0–3 Vol.% O$_2$, He balance, 450 °C | |
|      |          | 3) $^{15}$N$^{15}$O/CH$_2$/O$_2$/He→$^{15}$N$^{15}$O/CH$_2$/O$_2$/He | 1.2 Vol.% NO, 3 Vol.% O$_2$, He balance, 450 °C | |
|      |          | 4) $^{15}$N$^{15}$O/CH$_2$/O$_2$/He→$^{15}$N$^{15}$O/CH$_2$/O$_2$/He | 0.6 Vol.% NO, 0.75 Vol.% CH$_3$, 0.15–3 Vol.% O$_2$, He balance, 450 °C | |
| 17   | (5.0 wt.%)La$_2$O$_3$ (95 wt. %) | CaO | active chemisorbed NO species promoted via oxygen vacant sites in Ca$^{15}$-doped La$_2$O$_3$ | [24] |
|      |          | 1) $^{15}$NO/CH$_2$/O$_2$/He→$^{15}$NO/CH$_2$/O$_2$/He |        | |
|      |          | 0.6 Vol.% NO, 0.67 Vol.% CH$_3$, 5 Vol.% O$_2$, Ar balance, 550 °C |        | |
|      |          | 5) NO/CH$_2$/O$_2$/He→$^{15}$NO/CH$_2$/O$_2$/He |        | |
|      |          | 0.3 Vol.% NO, 0.4 Vol.% CH$_3$, 3.0 Vol.% O$_2$, He balance, 450 °C |        | |
|      |          | 4) NO/CH$_2$/O$_2$/He→$^{15}$NO/CH$_2$/O$_2$/He |        | |
|      |          | 0.95 Vol.% NO, 1.1 Vol.% CH$_3$, 5.0 Vol.% O$_2$, He balance, 450 °C |        | |
| 18   | (1.0 wt.%)Pt/SiO$_2$ | NO reduction by CH$_2$ | N$_2$O as the isotopically first product and N$_2$ as the isotopically second | [24] |
|      |          | 1) $^{15}$NO/CH$_2$/O$_2$/He→$^{15}$NO/CH$_2$/O$_2$/He |        | |
|      |          | 1.63 Vol.% NO, 0.89 Vol.% C$_2$H$_6$, 8.8 Vol.% O$_2$, Ar balance, 225 °C |        | |
During NH$_3$–SCR reaction the V-ONH$_4$ species can react with NO to form N$_2$ [Eqs. (14)]:

\[
\text{ONH}_4\text{OH} + \text{NO}(g) \rightarrow \text{N}_2 + \text{H}_2\text{O} + 2\text{H}_2\text{O}.
\]

The transient isotopic studies strongly suggest that replenishment of oxygen vacancies takes place by gas-phase O$_2$ and to a lesser extent by diffusion from the lattice oxygen.\(^{[37,38]}\) Together with NH$_3$–SCR, they investigated NH$_3$ oxidation at 400 °C.\(^{[38]}\) N$_2$ and/or N$_2$O were believed to be formed from two NH$_3$, which must remain on the V$_2$O$_5$ surface for a considerable length of time after the gas-phase has been replaced by $^{15}$NH$_3$. There was neither cross labeled N$_2$ nor N$_2$O, i.e., $^{14}$N$^{15}$N nor $^{15}$N$^{15}$NO. Otherwise, Efstathiou et al.\(^{[21,26]}\) studied NH$_3$ oxidation over (3.6, 9.0 wt.%) V$_2$O$_5$/TiO$_2$. Figure 3 shows the obtained responses of $^{15}$N, $^{14}$N$^{15}$N and $^{15}$N$_2$ isotopic species. They claimed that the difference in the time of appearance of the maximum in the rate formation of $^{14}$N$^{15}$N (0.67 or 6.4 min) demonstrate that the intrinsic site reactivity associated with adsorbed NH$_3$, e.g., V-ONH$_4$, is influenced by the V$_2$O$_5$ loading (3.6 or 9.0 wt.%) deposited on TiO$_2$.\(^{[23]}\)

According to the proposed reaction scheme,\(^{[37,38]}\) direct ammonia oxidation takes place on the basal planes of the V$_2$O$_5$ crystals. Thus, the surface coverage and turnover frequency values obtained for N$_2$ and/or N$_2$O were remarkably similar for the applied catalysts – V$_2$O$_5$–D (having preferential exposure of the side planes) and V$_2$O$_5$–M (having preferential exposure of the (010) basal plane). The samples varied in the NO transient values (not quantified for V$_2$O$_5$–D due to low values obtained for the NO formation). The sites that lead to NO formation appear to be different (active in a rapid insertion of lattice oxygen once the NH$_3$ adsorbs on these sites; residence time of 0.1044 s) from the ones that lead to N$_2$ and/or N$_2$O formation (residence time of 13.57–17.42 s). Furthermore, NO produced from NH$_3$ oxidation using the lattice oxygen could further react with NH$_3$ according to nowadays widely accepted the internal (in-situ) selective catalytic reduction (i-SCR) mechanism for NH$_3$ oxidation.\(^{[65,66]}\) Besides the application of SSITKA, also, the temporal analysis of products (TAP) has been applied in a limited number of studies concerning the ammonia oxidation. In particular, Pérez-Ramírez et al.\(^{[67,68]}\) investigated the sequence of steps in NH$_3$ oxidation at high temperatures to give NO, which is one of the stages in nitric acid production over PGM (Pt, Pd, Rh) wires or oxides (FeO$_x$, CrO$_x$, and CeO$_x$). The authors studied primary (NH$_3$ + O$_2$) and secondary (NH$_3$ + NO) interactions over PGMs at 900 °C using different C(NH$_3$):C(O$_2$) and C(NH$_3$):C(NO) ratios. NO was found as a primary reaction product, while N$_2$ and N$_2$O originated from consecutive NO transformations. The decrease in the C(NH$_3$):C(O$_2$) ratio effectively minimized the formation of N$_2$O and N$_2$ over the PGMs.\(^{[68]}\) Furthermore, they found that NO was the primary product of NH$_3$ oxidation also for oxides.\(^{[69]}\) Multi-pulse NH$_3$ experiments in the absence of gas-phase O$_2$ revealed that surface lattice oxygen of the studied oxides participated in NH$_3$ oxidation to NO. However, the formation of NO depended on the nature of the oxide. On the other hand, Olloffson et al.\(^{[70]}\) investigated the reaction mechanism of NH$_3$–SCO over (20.0 wt.%):CuO/Al$_2$O$_3$ (1.0 wt.%):Pt/Al$_2$O$_3$ and (1.0 wt.%):Pt/20 wt.%:CuO/Al$_2$O$_3$. The pump-probe experiments with alternate pulses of NH$_3$ and O$_2$ revealed the predominant formation of N$_2$ at the O$_2$ pulse on Pt/CuO/Al$_2$O$_3$ and the NH$_3$ pulse on Pt/Al$_2$O$_3$ or CuO/Al$_2$O$_3$. NH$_3$–NO$_2$ alternate pulsing indicated that the reaction between formed NO$_2$ (intermediate) and NH$_3$ species yielded N$_2$ over Pt/Al$_2$O$_3$ and CuO/Al$_2$O$_3$. Over Pt/CuO/Al$_2$O$_3$, most N$_2$ was formed by the NH$_3$ oxidation involving two NH$_3$ species, while reaction takes place at the Pt/CuO phase boundary between NH$_3$ species being adsorbed on CuO and oxygen on Pt sites. Additionally, the alternate pulsing of NH$_3$ and NO over preoxidized samples excluded NO as an intermediate, which is in contrast to studies of Burch and Southward\(^{[70]}\) or Gang et al.\(^{[71]}\) over Pt/CuO/Al$_2$O$_3$ or Ag/CuO/Al$_2$O$_3$, respectively. Certainly, SSITKA application - combined with other techniques (e.g., DRIFTS), over a broad

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**Figure 3.** Dimensionless transient response curves of $^{14}$N$_2$, $^{15}$N$^{15}$N and $^{15}$N$_2$ gases obtained during steady-state tracing of NH$_3$ oxidation reaction at 350 °C over a) (9.0 wt.%) and b) (3.6 wt.%)V$_2$O$_5$/TiO$_2$. Reprinted from \(^{[10]}\) with the permission of Elsevier.
range of catalysts could provide mechanistic insight of NH₂-SCO in real-time and conditions.

2.2. NO reduction by H₂

The effective NO reduction by H₂ in slight excess of O₂ over Pt/Al₂O₃ was firstly published in 1971 by Jones et al.[72] Research progress in the selective catalytic reduction of NOₓ by H₂ in the presence of O₂ was given by Liu et al.[49,50] Royer et al.[73] or Nova and Tronconi.[74] Especially Pt-based catalysts, including Pt/SiO₂, Pt/Al₂O₃, Pt/mesoporous silica (MCM-41, Al-MCM-41, etc.), Pt/zeolite, Pt/peorvskite, Pt/Al₂O₃-ZrO₂, Pt/MgO-CeO₂ etc. (also promoted with Na, Mo and/or W), are reported to be active at relatively low-temperatures (65–200 °C) while indicating also a high yield of N₂O. Burch et al.[31,32,34,40] studied H₂–SCR over (5.0 wt.%Pt/SiO₂ by SSITKA experiments. They reported that N₂O and/or N₂ appeared as the isotopically first product (with the lowest residence time on the catalysts relative to all products) and the last product, respectively.[31,34] The increase in temperature from 60 to 83 °C resulted in a higher N₂ production due to an increase in the concentration of sites (from 5.1 to 7.6 μmol g⁻¹) active for the production of N₂, together with a decrease of their mean surface residence time (from 64 to 42 s±0.5 s). The surface coverage of intermediates leading to N₂ was higher (0.06–0.10) than that of intermediates leading to N₂O (0.01–0.02).[34] ¹⁴N¹⁴N was still formed for a considerable time after all traces of gaseous ¹⁵NO was removed (Figure 4). The production of N₂O required gas-phase or weakly adsorbed NO.[31] The promotion of Pt/SiO₂(Al₂O₃) with Na₂O delayed the desorption of NO and causes a parallel increase in the decay time for the labeled N₂O. Furthermore, the addition of MoO₃ to these catalytic systems induced substantial increases in the concentration of surface species leading to N₂.[40] Further, a mathematical analysis (Temporal Redistribution of Isotopically Labeled Molecules of Product – TRIMP, i.e., the function y(i), the deviation from statistical isotopic distribution within the product molecules) of the profile shape allowed the recognition of the possible paths of the intermediates to the final products (Figure 5).[32,34] The authors suggested that formation of N₂ (in an extent of 85%) was the result of the interaction of two different NO₃ species (a weakly chemisorbed NO named as NO₃_ads and NO₃_ads), while that of N₂O was the result of two similar in nature NO₃ species (Eqs. (15–16)):

\[
\begin{align*}
N_2(ads) + NO_{(pre-ads)} & \rightarrow O_{(ads)} + N_2, \quad (15) \\
NO_{(pre-ads)} + NO_{(pre-ads)} & \rightarrow O_{(ads)} + N_2O. \quad (16)
\end{align*}
\]

This mechanism was supported by the density functional theory (DFT) studies.[75] The surface coverage of the active NO₃ intermediate species that lead to N₂ formation is considerably larger than that leading to N₂O. However, the chemical

Figure 4. Normalized product responses following the replacement of ¹⁴NO/Ar with ¹⁵NO in the reaction stream over (5 wt.%Pt/SiO₂. Reprinted from[31] with the permission of Elsevier.

Figure 5. The network of NO conversion into N₂O and N₂ over (5.0 wt.%Pt/SiO₂ in the NO/O₂/H₂ reaction as derived from SSITKA analysis. Reprinted from[31,34] with the permission of Elsevier.
structure of the active and/or inactive (spectator) NO₃ species was unidentified, as an effect of limitation of SSITKA.[46] The two different in the chemical structure active NO₃ species were identified by Costa and Esfathilou.[13] Thus, NO₃_presh and NO₃_ads. Placed by Burch et al.[34] were recognized as nitrosyls (Pt-NO₂⁺, IR band at 1900 cm⁻¹) and unidentate nitrates (and Pt-NO₃, IR band at 1480 cm⁻¹) adsorbed on Pt, respectively, through a combination of SSITKA and in situ DRIFTS over Pt/ SiO₂. The unidentate nitrates on Pt (IR band at 1620 cm⁻¹) were found to be spectators. Contrary to the results reported by Burch et al.[34] they suggested that the same active NO₃ precursor species must be involved in both N₂ and NO formation pathways [33]. For Pt/La₂O₃CeO₂MnO₃ the active NO₃ species (M-NO₃, nitrosyls, IR band at 2220 cm⁻¹) and M–(NO)-(O)–M, bidentate nitrates, IR band at 1540 cm⁻¹) are populated on the metal-support inter-phase region. 8.10 μmol g⁻¹ (0 = 1.74) of these active NO₃ species (81.5% leading to the formation of N₂) was found for Pt/La₂O₃CeO₂MnO₃ (compared to 3.04 μmol g⁻¹ (0 = 0.65) obtained for Pt/SiO₂).[35] The active precursor intermediate NO₂ species (14.4 μmol g⁻¹, 0 = 3.1) that lead to the formation of N₂ and N₂O over (0.1 wt.%Pt/MgO-CeO₂)[36] are located in the vicinity of Pt-CeO₂ (nitrosyls coadsorbed with nitrates on adjacent Ce₆O₇−: oxygen anion site pair) (IR band at 2220 cm⁻¹) and Pt-MgO support interface region (IR band at 1540 cm⁻¹). The chemical structure of the second active NO₃ species depended on the temperature and appeared as bidentate or monodentate nitrates (NO₃⁻: below 200 °C) or chelating nitrates (NO₃⁻: above 200 °C). The inactive adsorbed NO₃ appeared at the Pt metal surfaces and the MgO-CeO₂ support.[37,42] Chelating nitrite species (7.2–17.5 μmol g⁻¹, 0 = 1.8–4.4 at 200–300 °C) were found as the active intermediate over Pt/CeO₂ZrO₂O₂ω, whereas nitrosyls, monodentate and bidentate nitrates were considered as spectators.[44] The presence of H₂O in the feed resulted in a 25% decrease in the active NO₃ intermediate species and thus, partly explaining the significant drop in the catalytic activity during H₂–SCR. Based on the 18O SSITKA-MS experiments they found that for Pt/SiO₂ and Pt/La₂O₃CeO₂MnO₃,[34] H₂–SCR toward N₂O formation involves a reaction path of NO oxidation on Pt with the participation of gaseous O₂. However, it was not the case over Pt/MgO-CeO₂.[37,41]–[44]

Concluding, mainly Pt-containing catalysts were investigated in H₂–SCR by the combination of SSITKA-DRIFTS. The chemical structure of NO₃ adsorbed precursor intermediates as well as their abundance (i.e., the concentration of surface intermediates and their site coverage on the surface) significantly varied among applied catalysts compositions and applied temperatures.

2.3. NO reduction by CH₄ or C₃H₆

Starting from the pioneering work of Held et al.[76] and Iwamoto et al.[77] over Cu-ZSM-5, the reduction of NO₃ by hydrocarbons under strongly oxidizing conditions (HC₅–SCR) has been extensively studied.[78–88] Methane being the most abundant hydrocarbon in the form of natural gas offers a very attractive alternative for NO₃ reduction. CH₄–SCR was investigated mainly over zeolites (e.g., Co–CHA, Co–RTH, Co–UFI)[89] supported noble metals (e.g., Ag/Al₂O₃, Pt/Al₂O₃[90,91], and metal oxides (e.g., CoO₂/γ-alumina, CoO/ZrO₂(SO₄)₂[34,92]). Kumthekar and Ozkan[93,94] investigated CH₄–SCR over Pt/TiO₂ with palladium primarily in metallic form. They claimed that CH₄–SCR likely consists of NO–CH₄ reaction, CH₄ oxidation and NO decomposition proceeding simultaneously on the surface. The extent of each reaction was determined by the oxidation state of Pd on the surface and of the reaction parameters. Based on the 14N³º/O²⁻/He → 15N¹⁸º/O²⁻/He or CH₄¹⁸ºNO/O²⁻/He→CH₄¹⁴ºNO/O²⁻/He experiment, they claimed two different intermediates/routes for the formation of products. N₂ and NO (i.e., ¹⁵N₂, ¹⁴N₂O, ¹⁴N₂O, ¹⁵N₂O and ¹⁵N₂O), were formed, but there were no cross-labeled species. The catalyst's surface was capable of combining two NO molecules through a dimeric intermediate to give a N₂O molecule. N₂ and CO₂ were found to be mainly formed through direct participation of CH₄ with a methyl dinitrosyl species acting as an intermediate.[92]

Sadovskaya et al.[27,95,96,97,98] focused on the formation of NO₃ adsorbed species in the absence and the presence of O₂ over Co-ZSM-5. Firstly, they investigated the dynamics of isotopic exchange between the NO+O₂ without CH₄ (Table 1, pos. 16, doubly labeled nitric oxide: ¹⁴N²ºNO→¹⁵N²ºNO in 0.6–1.2 Vol.% NO/O₂/He mixtures at 450 °C).[99] Based on previously reported in situ DRIFTS analysis,[100] nitronyls, NO₂⁺ species and nitrite complexes were distinguished on Co sites. The rate of ¹⁵N exchange with gaseous NO decreased as follows: nitronyrls ≫ NO₂⁺ species > nitrite complexes. The authors proposed that CH₄–SCR in the presence of O₂ proceed with the participation of NO₂⁺ (formed at the interface between oligonuclear cobalt oxide species and hydroxyl groups of the zeolite; r = 0.020·10⁻¹⁹ molec g⁻¹ s⁻¹) and NO₂⁻ nitrite complexes (on larger cobalt oxide particles located outside the zeolite channels; r = 0.008·10⁻¹⁹ molec g⁻¹ s⁻¹), Figure 6.[98] Mononitrosyl species possibly participated in the overall reaction by interconversion to nitrate species.[96,97] The active species vary among applied catalysts. E.g., Anastasiadou et al.[92] found an enhanced intrinsic reaction rate of NO reduction by CH₄ over (5.0 wt.%La₂O₃–95 wt.%)CaO (TOF = 8.5·10⁻¹ s⁻¹) compared to pure CaO (TOF = 3.6·10⁻¹ s⁻¹). Based on ¹⁴NO SSITKA/DRIFTS, they revealed the formation of oxygen vacant sites in CaO–La₂O₃, which promoted the formation of active chemisorbed NO₃ species (NO₃⁻), thus facilitating CH₄–SCR. Bridged

Pathway 1

\[ \text{[z-*NO₂CH₃]} \rightarrow \text{[z-*NOCH₃]} + \text{H₂O} \]

Pathway 2

\[ \text{[z-*NO₂CH₃]} \rightarrow \text{[z-*NOCH₃]} + \text{H₂O} \]

Figure 6. Two main parallel pathways for CH₄-SCR over Co-ZSM-5. Note that CH₄ and NO + O₂ addition along the proposed pathways are likely to proceed via adsorbed species: for CH₄ = \{CH₄* \}, \{z-*C\}, and \{z-*O\}, and NO + O₂ = mononitrosyl and activated oxygen over Co nanoclusters, respectively. Reprinted from [92] with the permission of Elsevier.

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nitrates were considered as spectators. Clearly, the application of SSITKA-DRIFTS leads to the recognition of real intermediates and/or spectators in real-time and conditions (e.g., applied catalysts, reactant feed concentrations, temperatures, etc).

3. Summary and Outlook

Despite intensive studies on reaction mechanism for SCR (NH$_3$-SCR or NH$_3$-SO$_2$, H$_2$-SCR, CH$_4$-SCR or CH$_4$-SCR) many features of the process remain unclear and controversial. The examples reported here show that combining SSITKA and DRIFTS can greatly benefit the understanding of the mentioned catalytic reactions and under real conditions. Coupling SSITKA with in situ DRIFT spectroscopy makes available information on the surface coverage of active and inactive (spectators) species under reaction conditions and correlation of particular surface intermediates to given reaction products. It should be expected to be applied with increasing frequency in the environmental/automotive catalysis. Although complete testing of the catalysts would certainly require examining the reduction in the presence of a varied concentration of O$_2$, H$_2$O, CO$_2$ and even SO$_2$.

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Conflict of Interest

The authors declare no conflict of interest.

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