Effects of CO, H₂ and C₃H₆ on Cu-SSZ-13 Catalyzed NH₃-SCR

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Abstract

We investigated the steady-state and transient effects of reductants (CO, H₂ and C₃H₆) on NO₂ reduction, NH₃-SCR (selective catalytic reduction), NH₃ adsorption and oxidation, and N₂O production on a Cu-SSZ-13 monolithic catalyst. The three reductants affect to different extents the standard SCR (NO + NH₃ + O₂), fast SCR (NO + NH₃ + NO₂), and slow SCR (NH₃ + NO₂). This study underscores the importance of accounting for the impact of reducing agents on conventional NH₃-SCR reaction mechanism when SCR catalyst is subjected to either rich regeneration of integrated systems (LNT + SCR, SCR on DPF) or cold-start. Propylene is most effective in promoting NO₂ reduction to NO by formation of organic intermediates. CO effectively reduces nitrates to nitrites that then react with NO₂, releasing NO. H₂ can follow a similar pathway as CO but is less effective. In addition, H₂ can also enable a H₂-based SCR pathway through the reduction of Cu cations to Cu⁰ which then catalyze the NO_x reduction. This pathway is particularly evident at high temperatures and low O₂ levels. As for NH₃-SCR reactions, propylene competes with NH₃ for adsorbed NO₂, which generates NO and thus increases the NO/NO_x ratio. This leads to the dominance of either fast or standard SCR for a slow SCR (NH₃ + NO₂) feed condition when C₃H₆ is present. CO has only a minor effect on both standard and fast SCR but a promoting effect on slow SCR. The ineffective reduction of NO₂ to NO by H₂ at low temperature (T < 250 °C) results in a negligible effect on slow SCR. In contrast to steady-state operation, lean/rich cycling enhances cycle-averaged NO_x conversion for each of the NH₃-SCR reactions when adding either C₃H₆ or a CO + H₂ mixture in the rich phase. A decreased N₂O generation rate from the slow SCR reaction is observed when any of the three reductants are present due in part to their reaction with ammonium nitrates.

Keywords: NH₃-SCR, Cu-SSZ-13, CO, H₂, C₃H₆, LNT+SCR

1. Introduction

Lean-burn gasoline and diesel engines achieve a higher fuel economy than stoichiometric gasoline engines. Their use will enable vehicle manufacturers to meet the stringent 2017-2025 US EPA greenhouse gas and NHTSA (National Highway Traffic Safety Administration) fuel economy standards [1]. A major challenge of lean-burn application is the reduction of nitrogen oxides (NO_x ; $\text{NO} + \text{NO}_2$) in a net oxidizing environment. Ever-tightening Tier 3 and LEV III emission regulations exacerbate this technological challenge [2]. Two commercialized de NO_x technologies that meet the current emission standards are NO_x storage and reduction (NSR) and selective catalytic reduction (SCR). The SCR technology reduces NO_x to N_2 by reaction over vanadium-based or transition metal exchanged zeolite catalysts with NH_3 generated from urea hydrolysis. SCR is the leading de NO_x solution for mid- or heavy-duty vehicles and can achieve over 95% de NO_x efficiency at practically relevant space velocities. It requires an onboard urea storage and delivery system with a minimum urea dosing temperature requirement of $\sim 200^\circ\text{C}$. This limits its function during cold-start or low-load conditions. For light-duty lean-burn vehicles, NSR is preferred. It involves the storage of NO_x on a lean NO_x trap (LNT) catalyst under lean conditions, followed by a short, rich regeneration by a mixture of CO , H_2 and hydrocarbons (HC) [3]. The LNT catalyst requires precious group metals (PGM) to achieve a high NO_x conversion. However, it is not as selective as SCR, producing byproducts such as N_2O and NH_3 .

The integration of SCR with NSR (or equivalently LNT) has aroused much interest [4-6]. One example is the LNT + passive SCR system wherein the SCR catalyst utilizes NH_3 produced by the upstream LNT during rich purges to achieve incremental NO_x reduction. This system lowers the cost by the reduction of the PGM loading required for the LNT and elimination of the urea injection for the SCR system [7]. The overall NO_x conversion is still mostly confined in the LNT, which decreases at high temperatures ($> 400^\circ\text{C}$) due to decreased NO_x storage capacity and NH_3 yield. A new LNT + active SCR system with urea dosing was proposed by researchers from SwRI [8] and Hyundai [9]. It uses a LNT to overcome the SCR cold-start NO_x emission, when the temperature is too low for urea dosing. The combined system has been demonstrated to meet the LEV III limits. It is a promising solution for LEV III-compliant diesel vehicles [10].

In contrast to the stand-alone urea-SCR system designed to operate with a lean exhaust, the combined LNT+SCR is inevitably exposed to a rich exhaust condition during the LNT regeneration. Deep rich purges are preferred to promote NH_3 generation by the LNT. This may generate relatively high levels of CO, H_2 and HC slippage to the SCR catalyst [11, 12]. A recently-commercialized SCR on-filter (SCRF) technology comprises a diesel particulate filter (DPF) that is coated with SCR catalyst and is positioned in close proximity to the engine to enable fast SCR light-off. The SCR component encounters a rich environment during the periodic DPF regeneration events [13]. Even the SCR-only system may be exposed to a rich feed under certain conditions such as cold-start period, extended vehicle idling, engine malfunction, or degraded upstream diesel oxidation catalysts (DOC) [14, 15]. All of these scenarios raise questions regarding the potential impact of rich reducing agents on the performance of the SCR catalyst.

Previous studies of the impact of various reductants on NH_3 -SCR performance over metal-exchanged zeolites have mainly focused on HC species poisoning. It is well known that stored HC on zeolites can have a detrimental effect on both the SCR catalyst performance and its durability [16]. He et al. reported a negative effect of C_3H_6 due to carbon deposits during standard SCR ($\text{NO} + \text{NH}_3 + \text{O}_2$) over a Fe-beta zeolite [17]. Heo et al. attributed the competitive adsorption of NH_3 and C_3H_6 on the catalyst as well as undesired NH_3 consumption by side reactions to the decreased NH_3 -SCR activities of Fe- or Cu- ZSM-5 [18]. Epling et al. compared the effects of C_3H_6 and dodecane ($\text{n-C}_{12}\text{H}_{26}$) exposure over two Cu-exchanged zeolite catalysts; one was a small-pore zeolite (Chabazite framework, CHA) while the second was a standard large-pore Cu-BEA zeolite [19]. The Cu-CHA had a much better resistance to HC poisoning than the Cu-BEA by effectively suppressing HC adsorption and coke formation. A slightly decreased standard SCR activity was observed when adding C_3H_6 to the gas fed to the Cu-CHA [19]. This was attributed to formation of partial oxidation intermediates. In a follow-up study, Kumar et al. found that even a small-pore zeolite could store non-negligible amounts of carbonaceous deposits from either short- or long-chain HCs via an oxygen-dependent, thermally-activated storage process [15]. All the above studies were conducted with continuous exposure of the SCR catalysts to a HC. Wang et al. [20] and Kim et al. [21] reported that under lean/rich cyclic conditions, the enhanced cycle-

averaged NO_x conversion over a Cu-CHA catalyst by C₃H₆, was attributed to the mitigation of HC poisoning and HC-SCR reactions.

The factors accounting for the impact of HC on NH₃-SCR over SCR zeolite catalysts include competitive adsorption, undesired NH₃ consumption, formation of partially oxidized intermediates and operating conditions (continuous or cyclic). A clear elucidation requires a systematic analysis. However, to date only a few studies investigated the effects of other reducing reagents like CO and H₂ on NH₃-SCR zeolite catalysts. Huang et al. studied the deactivation of Cu-zeolites by reductive hydrothermal aging [14]. They found that extended exposure to a CO/H₂ mixture at 650 °C resulted in permanent catalyst deactivation due to the sintering of Cu⁰ from the reduction of isolated Cu²⁺ cations. Exposure to C₃H₆ under the same conditions resulted in a reversible deactivation after coke removal. Smith et al. [22] recently reported that compared to C₃H₆, CO and H₂ had a negligible effect on the NH₃-SCR chemistry over an Fe-zeolite catalyst, with the main contribution being a slight promotion of NO₂ reduction to NO.

To the best of our knowledge, the effects of a reductant mixture containing CO, H₂ and C₃H₆ on the SCR performance of a small-pore Cu-chabazite catalyst under either steady-state or cyclic operations have not been systematically studied. To this end, in this study we examine the effects of each reductant through temperature ramp, step-response and cyclic experiments. The results can help in the interpretation of NH₃-SCR on Cu-CHA catalysts when subjected to rich exhaust exposure.

2. Experimental

2.1 Catalyst

A Cu-SSZ-13 SCR catalyst having a CHA framework was provided by BASF (Iselin, NJ). The SCR sample had a cell density of 400 cpsi and an estimated washcoat loading of about 2.4 g/in³ with ca. 2.5 wt.% Cu loading. For bench reactor evaluation, a core sample was prepared (D=0.8 cm, L=1.0 cm, 28 channels). Prior to the reactor tests, the catalyst was de-greened at 500 °C for 5 hours in a feed mixture containing 5% O₂, 2.5% H₂O, 2% CO₂, and balance of Ar.

2.2 Temperature ramp experiments

The bench-scale reactor set-up comprised a gas supply, tubular monolith reactor, and analytical and data acquisition systems. Gas flow rates were controlled by mass flow controllers (MKS Inc.) before entering the inline static mixer. Water was fed by a syringe pump (ISCO Model 500D) and vaporized in a heated line. A LabTech interface controlled the switching valve and mass flow controllers for the feed streams. The monolith catalyst was wrapped with Fiberfrax® ceramic paper and inserted inside a quartz tube (40.6 cm long, 1.27 cm outer diameter) mounted in a tube furnace coupled to a temperature controller. The temperature inside the reactor was measured by two 0.5 mm type-K stainless steel sheathed thermocouples (Omega Engineering Inc.). One placed 0.5 cm in front of the monolith measured the feed temperature. The second measured the temperature in the middle of the center monolith channel. The gaseous effluent concentrations of NO, NO₂, N₂O, NH₃, CO, CO₂ and H₂O were measured by a calibrated FT-IR spectrometer (Thermo-Nicolet, Nexus 470).

The SCR catalyst was exposed to a constant feed composition at 500 °C to establish a steady state before the temperature ramp experiments. The downward temperature ramp to 200 °C was conducted at a rate of -2 °C/min to minimize the complicating effect of NH₄NO₃ formation. The ramp rate was sufficiently slow to avoid thermal hysteresis effects and to obtain essentially steady-state results. [Comment: The downward ramp was found to be more effective in this regard than an upward ramp. For example, the NO₂ SCR reaction (NO₂+NH₃) is hard to reach steady-state at low temperature (~ 200 °C) due to the gradual accumulation of NH₄NO₃ on the catalyst; this process deactivates the catalyst and makes it difficult to differentiate among the effects of different reducing agents.] In some experiments, a step-response method was employed in order to evaluate both the transient and long-term response to gas concentration changes.

The feed gas composition for the baseline NH₃-SCR reactions comprised 500 ppm NH₃ and 500 ppm NO for standard SCR (NO/NO_x=1; 4NO + 4NH₃ + O₂→4N₂ + 6H₂O), 250 ppm NO and NO₂ for fast SCR (NO/NO_x=0.5; NO + NO₂ + 2NH₃→2N₂ + 3H₂O) and 500 ppm NO₂ for slow SCR (NO/NO_x=0; 3NO₂ + 4NH₃→3.5N₂ + 6H₂O), in 0% or 5% O₂ (as specified) in a carrier gas of 2.5% H₂O, 2% CO₂ and balance Ar, at a space velocity of 120,000 hr⁻¹. A reductant feed of either 1% CO or 1% H₂ or 500 ppm C₃H₆

was introduced as specified. The amount of C₃H₆ (500 ppm) was lower than that of CO (1 %) or H₂ (1%) on a total reductant basis (the amount of O species that can be consumed by reductants); i.e., 500 ppm C₃H₆ can consume 4500 ppm O species, while 1% of either CO or H₂ can consume 1% O species.

2.2 Lean/rich cycling experiments

Lean/rich (30/5s) cycling experiments were conducted over the SCR catalyst. Table 1 describes the baseline cycling conditions. A reductant of either 1% CO or 1% H₂ or 500 ppm C₃H₆ was added to the baseline rich phase. The feed temperature was increased from 200 to 450 °C in steps of 50 °C. It typically took approximately ~10 min to reach a periodic steady state. At each temperature the cycle-averaged NO_x (NO+NO₂) conversion for a particular operating condition was determined from the average of the final ten periodic cycles. The fractional NO_x conversion was calculated by

$$X_{NOx} = 1 - \frac{\int_0^{\tau_T} [F_{NO}(t) + F_{NO_2}(t)] dt}{\int_0^{\tau_T} [F_{NO}^i(t) + F_{NO_2}^i(t)] dt}$$

Here τ_T is the duration of a lean-rich cycle. $F_{NO}^i(t)$ and $F_{NO_2}^i(t)$ are the NO and NO₂ feed rates and $F_{NO}(t)$, $F_{NO_2}(t)$ are the effluent molar flow rates (mole/s).

2.3 Temperature-programmed desorption (TPD) experiments

Two types of TPD experiments were performed. The first evaluated the effects of the three reductants on the NH₃ storage capacity. The catalyst was exposed to 500 ppm NH₃ in a carrier gas with and without the presence of a reductant mixture containing 1% CO, 1% H₂ and 500 ppm C₃H₆ at 200 °C for 30 mins, followed by another 30-min flush with carrier gas. The sample was then heated in carrier gas at a rate of 7.5 °C/min up to 500 °C. The second type studied the surface reactions between NH₄NO₃ and reducing agents. An equal amount of NH₄NO₃ was first loaded by co-feeding 500 ppm NH₃ and 500 ppm NO₂ to the SCR catalyst at 200 °C for 30 mins, followed by a 30-min purge with carrier gas. The sample was then heated at 15 °C/min to 400 °C in a carrier gas (baseline), or in a

mixture with either 1% CO or 1% H₂ or 500 ppm C₃H₆. Prior to each experiment, the catalyst was exposed to 5% O₂ in a carrier gas at 500 °C for 1h.

3. Results and discussion

3.1 NO and NO₂ reactions with CO, H₂ and C₃H₆

Fig 1 compares the NO conversion during the reaction of NO with CO, H₂ or C₃H₆ under both anaerobic and aerobic conditions. CO shows negligible NO conversion over the entire temperature range of 200 to 500 °C, regardless of the presence of O₂. Although C₃H₆ is inert to NO under anaerobic conditions, the presence of O₂ enables the reduction of NO to N₂ via a HC-SCR pathway, which involves propene partial oxidation intermediates to react with NO. On the other hand under anaerobic condition, H₂ begins to effectively reduce NO above 350 °C, with over 90% NH₃ selectivity. Copper-based catalysts have been reported to catalyze H₂-SCR reaction with metallic copper (Cu⁰) as the catalytically active site [23]. Cu-exchanged SSZ-13 is considered to contain isolated Cu cations as active centers. Thus, the first step in H₂-SCR by Cu-SSZ-13 likely involves the reduction of Cu ions to Cu⁰. H₂-TPR method has been widely utilized to assess the reducibility of various copper species on Cu-CHA catalysts. For example, H₂ is capable of reducing Cu ions like Cu-dimers to Cu⁰ at temperatures above ~350 °C [24], which coincides with the light-off temperature of NO reduction by H₂ in Fig. 1a. This supports the speculation of a stepwise mechanism involving Cu⁰ formation followed by NO hydrogenation to NH₃.

The addition of O₂ inhibits the reaction of NO with H₂ as seen in Fig. 1b. This is attributed to two factors. First, Cu⁰ catalyzes the oxidation of H₂ by O₂ which reduces the H₂ available for NO reduction. Second, the excess O₂ inhibits the formation of Cu⁰ by oxidizing Cu⁰ to either Cu cations or CuO cluster [14], both of which result in less Cu⁰ available for NO adsorption and/or reduction.

Fig. 2a compares the NO₂ and NO_x conversions over a wide temperature range during the reaction of NO₂ with CO, H₂ or C₃H₆ in the absence of O₂. Fig. 2b shows the corresponding effluent NO and NO₂ concentrations over the same temperature range. C₃H₆ exhibits the highest reactivity with NO₂, leading to the lowest light-off temperature

(defined here as the temperature at which NO_x conversion is 50% of the maximum). NO₂ reduction by C₃H₆ begins at 200 °C and increases up to ~300 °C where it levels off at 100% NO₂ conversion and ~35% NO_x conversion. CO starts to reduce NO₂ at ~225 °C and plateaus at 100% NO₂ conversion and ~23% NO_x conversion at 350 °C. Although NO₂ reduction by H₂ is the least effective on the basis of having the highest light-off temperature, the NO_x conversion increases up to ~ 85% at 500 °C, in contrast to the plateaus observed for C₃H₆ and CO.

The NO and NO₂ effluent concentrations shown in Fig. 2b provide additional insights into the reactions of NO₂ with CO, H₂ or C₃H₆. NO₂ reduction to NO promoted by either CO or C₃H₆ occurs with concomitant and near-stoichiometric formation of NO. This is seen clearly at low temperatures; i.e. moles NO₂ consumed are equal to the moles NO produced. Both C₃H₆- and CO-assisted NO₂ conversion begin at 200 °C and reach 100% NO₂ conversion above 350 °C. It is worth noting that the N-balance is not closed at high temperatures in the baseline case. This is most likely due to the formation of some undetected gaseous HNO₃ that leaves the reactor.

The reaction of NO₂ with C₃H₆ was previously reported as part of the following HC-SCR pathway:

The overall HC-SCR reaction is given by:

Gorce et al. [25] proposed that organic nitro intermediates (denoted by R-NO₂) formed by the reaction of C₃H₆ and ad-NO_x species (R1), decompose to NO and oxygenates

(C_xH_yO_z, such as acrolein) (R2). In turn, the oxygenates serve as active intermediates that further react with NO₂ or NO+O₂ to proceed the HC-SCR pathway (R4).

Overall reaction (R3) accounts for the stoichiometric conversion of NO₂ to NO. It also explains the appearance of the plateau in the NO_x conversion for C₃H₆ in Fig. 2a, which coincides with the complete conversion of NO₂. That is, a lack of NO₂, which is required for reaction with oxygenates (R4), limits further NO_x conversion and results in the plateau.

We propose the following nitrate-related mechanism for CO:

The overall reaction (R7+R8) is given by

Nitrates formed by NO₂ disproportionation (R6) are reduced to nitrites by CO (R7), followed by their rapid reaction with NO₂, generating NO (R8). This reaction pathway was verified in a separate experiment when pulsing CO to the SCR catalyst initially contacted with NO₂ for 1 h at 300 °C (data not shown here). The instantaneous CO₂ release upon the feed of CO confirms the reactivity between nitrates and CO. This is discussed further below. Forzatti et al. [26] proposed a similar reduction of nitrates over a LNT catalyst by CO to form nitrites with evolution of CO₂.

Compared to CO and C₃H₆, H₂ is not as effective in the reduction of NO₂ to NO. For example, 95% NO₂ conversion is achieved at ~380 °C, somewhat higher than that for C₃H₆ (~300 °C) and CO (~350 °C). Note that a peak in the effluent NO concentration occurs at ~350 °C. The increasing NO concentration to the left of the peak is likely due to a similar NO₂ reduction pathway as for CO, with H₂ reducing nitrates to nitrites (R10)

that can further reduce NO₂ to NO (R8). This reaction pathway was verified by introducing H₂ to a pre-nitrated SCR catalyst at 300 °C. The nearly instantaneous production of H₂O, NO₂ and NO at the moment of H₂ admission agrees with the following proposed nitrate-related pathway.

The decreasing NO concentration above 350 °C, at which point the H₂-SCR of NO begins to light off as shown in Fig. 1a, is attributed to increased H₂-SCR activity. Based on the established mechanism for H₂-SCR, which involve the adsorption and dissociation of H₂ and NO_x over metallic metal sites [27], we expect that the following H₂-SCR pathway is favored over the above nitrate-related pathway at higher temperature range:

To examine the above pathways, a three-phase step response protocol was employed. As shown in Fig. 3, the protocol consisted of a NO₂ feed (500 ppm NO₂, Phase 1), followed by the addition of 1% H₂ in the absence (Phase 2) and presence (Phase 3) of 5% O₂ at 500 °C. During the Phase 1, NO₂ undergoes the thermal decomposition, producing NO. A sharp decrease in NO₂ concentration to nil with a corresponding steep increase in NO concentration occur upon the introduction of H₂ in Phase 2. the NO rapidly peaks and then decreases to a local minima at ~ 250 s entering Phase 2, followed by a gradual increase up to the 2450 s mark. The NO peak is attributed to the rapid reduction of accumulated surface nitrates to nitrites (R10) that then reduce NO₂ to NO (R8). Meanwhile, the formation of metallic copper sites which catalyze the H₂-SCR reaction, reduces the NO_x to N₂ and NH₃ (R11-16). The prolonged H₂ exposure results in a

sintering of metallic copper that is responsible for a gradual decrease in NO conversion from 750 to 2450 s. Huang et al. [14] reported that a high-temperature reducing treatment of Cu-zeolite catalysts by H₂ caused an irreversible sintering of Cu metals and thus the catalyst deactivation. Subsequent O₂ introduction in Phase 3, leads to a sharp increase in NO concentration. This confirms that the presence of O₂ inhibits H₂-SCR reaction as was shown by in Fig. 1b. In addition, NO₂ disproportionation (R6) is favored by the presence of O₂ to produce nitrates for the nitrate-related pathway. The inhibition of H₂-SCR pathway and the promotion of the alternative nitrate pathway results in a higher NO level under aerobic conditions.

3.2 The effects of CO, H₂ and C₃H₆ on NH₃ oxidation and storage

NH₃ storage plays a crucial role in the NH₃-SCR performance, especially at low temperatures. Thus, it is important to assess the effects of reducing agents on the NH₃ storage. Heo et al. reported that C₃H₆ competes with NH₃ for storage sites over Cu-ZSM-5, leading to inhibiting NO_x reduction [18]. Epling et al. reported negligible C₃H₆ adsorption on Cu-SAPO-34 under anaerobic conditions, indicating that C₃H₆ may not compete with NH₃ for adsorption on the active sites [19]. Kumar et al. showed that extended exposure of Cu-SAPO-34 to C₃H₆ in the presence of O₂ at temperatures between 200 and 400 °C decreased NH₃ storage capacity. This is attributed to the formation of carbonaceous deposits which block the storage sites [15]. Wang et al. reported the co-adsorption of C₃H₆ and NH₃ on Cu-SSZ-13 under anaerobic conditions with no apparent coupling between the two adsorbates [20]. Finally, no studies of the effect of CO or H₂ on NH₃ storage on Cu-CHA have been reported. Since H₂ and CO are considered as effective molecular probes in the characterization of various copper species over Cu-zeolite catalysts; i.e. H₂ can reduce the oxidation state of Cu ions, while CO can strongly adsorb onto Cu⁺ to form carbonyls [28], these may affect the NH₃ adsorption on Cu cations.

Fig. 4 shows NH₃ TPD profiles on Cu-SSZ-13 after being saturated at 200 °C with NH₃ in the presence and absence of CO, H₂ and C₃H₆. Two desorption peaks, one at ~275 °C and the second at ~ 400 °C, were observed during the temperature ramp; these can be assigned to NH₃ adsorbed on weak acid sites (Cu cation or extra-framework Al Lewis

sites) and stronger acid sites (Brønsted sites), respectively [29]. The near overlap of the two NH_3 desorption profiles indicates that addition of CO , H_2 and C_3H_6 has a negligible impact on both NH_3 storage capacity and the strength of different acid sites. These data suggests that none of the three reductants competes with NH_3 for the acid storage sites of the Cu-chabazite catalyst.

Ammonia oxidation is an undesired side reaction among the NH_3 -SCR reactions. It decreases the NH_3 available for NO_x reduction and can generate undesired byproducts, such as N_2O . Fig. 5 compares the NH_3 conversion in the presence of $\text{CO} + \text{H}_2$ and C_3H_6 . The data show that C_3H_6 inhibits the NH_3 oxidation by increasing the light-off temperature by about 50°C . This is attributed to the formation of partial oxidation intermediates that block the active sites; this is as evidenced by concomitant CO release above 300°C during a separate propene oxidation experiment shown in Fig. 6. CO and H_2 , slightly decrease NH_3 conversion between 300 and 350°C . This is probably due to the reduced copper oxidation state by CO and H_2 . For all NH_3 oxidation experiments, Cu-SSZ-13 exhibits very high N_2 selectivity ($> 98\%$) during the entire temperature range.

3.3 Steady-state effects of CO , H_2 and C_3H_6 on NH_3 -SCR reactions

3.3.1 Temperature ramp method

In the LNT+SCR application, the SCR catalyst encounters a NO_x stream with widely varying NO_2/NO_x ratio. As shown earlier, C_3H_6 , CO and H_2 promote the conversion of NO_2 to NO to different extents and thus affect the NO/NO_2 ratio. It is well known that the de NO_x efficiency of SCR catalysts is sensitive to the NO/NO_2 ratio, especially at low temperatures, with the highest NO_x conversion and/or N_2 yield achieved at an equimolar ratio of NO to NO_2 [30]. Thus, it is important to determine the effects of these reductants on SCR performance and the reaction mechanism.

Fig. 7a shows steady-state NO_x conversion during the standard SCR reaction in the presence of CO , H_2 , or C_3H_6 for temperatures between 200 and 500°C . The addition of either CO or H_2 has a negligible effect on baseline NO_x conversion in the low and intermediate temperatures, while slightly decreasing the high-temperature NO_x conversion. The inhibitory effect at high temperature may be due to the interference by

either H₂ or CO with the redox cycling between Cu²⁺ and Cu⁺ that is critical for standard SCR reaction on Cu/CHA catalysts [30]. C₃H₆ inhibits the NO_x conversion with the negative effect most pronounced in the medium temperature range (~350 °C). The small pore structure of the Cu-CHA catalyst restricts the oligomerization of the propene oxidation intermediates inside the channels of the zeolite, as reported by Epling et al. [19]. Thus, organic intermediates (C_xH_yO_z or C_xH_yO_zN_i) instead of coke play an important role in the blocking of active sites. Raj et al. reported that the formation of isocyanate species from the reaction of partially oxidized C3 species with NO may inhibit C₃H₆ oxidation over a Cu-SSZ-13 catalyst [31].

In situ DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) measurements were conducted to identify surface intermediates species over a Cu-SSZ-13 powder catalyst. Fig.8 shows the temporal DRIFTS spectra when exposing a NO_x pre-adsorbed SCR catalyst to a feed of 0.1% C₃H₆ + 1% O₂ at 200 °C. After 1h of pre-conditioning the catalyst by 500 ppm NO + 5% O₂, three intense bands were observed at 1575, 1610 and 1625 cm⁻¹. These can be assigned to the adsorbed NO₂ species, monodentate nitrates, and bidentate nitrates, respectively [32]. After feeding propene a temporal decrease in the intensity of the adsorbed NO₂ and surface nitrates peaks occurred, and four new bands at 1650, 2218, 2254 and 2278 cm⁻¹ gradually evolved. The dramatic spectral intensity of the surface NO_x species indicates a rapid reaction of surface NO_x species with propene. The band at 1650 cm⁻¹ may be assigned to a C=O bond vibration of acrolein [33]. But it may also be the C=C stretch band of propene or other intermediates bands that are close to 1650 cm⁻¹. The bands at 2218, 2254 and 2278 cm⁻¹ can be assigned to Cu⁺-NCO [34], R-NCO over zeolites [35] and R-CN [36], respectively. The appearance of all these bands confirms the formation of organic intermediates from the reaction between surface NO_x species and propene. In addition, a broad band formation is recorded at around 2168 cm⁻¹ assigned to CO adsorption to Cu cation [37]. This is consistent with CO as an incomplete oxidation product. The local minimum in NO_x conversion at ~380 °C in Fig. 7a is attributed to the increasing formation of partial oxidation intermediates, as evidenced by the CO release peak at the similar temperature region for C₃H₆ oxidation in Fig. 6. At temperatures above 420 °C, the poisoning effect of C₃H₆ is gradually reduced, since either intermediates or coke, if

formed, may be burned off. Reaction at high temperatures gradually becomes controlled by the supply of reductant since oxygen competes with NO_x for NH₃.

Fig. 7b shows that for the fast SCR reaction, H₂ has negligible effect on the baseline NO_x conversion at low temperatures. It moderately increases NO_x conversion at temperatures exceeding 350 °C, due to the contribution by the H₂-SCR. Both CO and C₃H₆ slightly decrease the NO_x conversion (by ~5%) for temperatures below 250 °C. At temperatures above 250 °C, CO has little effect while C₃H₆ decreases the NO_x conversion monotonically with temperature. In the absence of O₂ in the feed, the oxidation of C₃H₆ is minimal so the decreasing NO_x conversion cannot be attributed to the inhibitory effect of partial oxidation intermediates as for the standard SCR case, especially at high temperatures. To explain the decreasing NO_x conversion trend, consider the fast SCR pathway proposed by Tronconi et al. [38]:

As mentioned previously, surface-bound NO₂ rapidly reacts with C₃H₆ which produces oxygenates and NO (R3). The consumption of NO₂ by C₃H₆ decreases the rate of NO₂ disproportionation (R13). This decreases the production of nitrates (NO₃⁻) and thus a lower consumption of NO is encountered (R14). The net effect is to increase the NO/NO_x ratio. Thus, from a global reaction standpoint, C₃H₆ competes with NH₃ for NO₂, increasing the NO/NO_x ratio towards 1 and shifting the feed ratio from fast SCR to standard SCR. The absence of O₂ impedes the commencement of either standard SCR or HC-SCR pathway, thereby decreasing the NO_x conversion with increasing temperature.

In contrast, a NO_x conversion decrease is not observed when CO (or H₂) is present. This supports our earlier conjecture that CO-assisted NO₂ reduction occurs through the nitrates to nitrites (R7) rather than through the reaction of CO with gas-phase NO₂, which would generate NO. If the latter were the case, the increased NO/NO_x ratio would lead to the same inhibitory effect that was encountered for the C₃H₆ feed. Thus, CO affects the fast

SCR mechanism by competing with NO for nitrate reduction (R14) to nitrites, which rapidly react with NH_3 , producing N_2 . Smith et al. observed a similar effect of CO on fast SCR reaction over an Fe-zeolite catalyst, but attributed it to the much higher faster SCR reaction rate than the rate of CO-assisted NO_2 reduction [22]. Their explanation is plausible from a global reaction perspective without looking more deeply into the underlying reaction mechanism. NO is known to effectively reduce nitrates at much lower temperature, even at 100 °C over Cu-CHA catalysts as reported by Di et al. [32], while CO requires 200 °C as shown in Fig. 2b. It is reasonable to presume that NO is more competitive than CO in terms of nitrate reduction, thereby limiting the impact of CO on the fast SCR reaction.

Fig. 9 shows that for the slow SCR reaction (NO_2 -only NO_x feed), the addition of C_3H_6 or CO below 270 °C, enhances NO_x conversion while H_2 has negligible impact. The ineffective reduction of NO_2 to NO by H_2 at low temperatures, shown in Fig. 2b, explains the negligible increase in low-temperature NO_x conversion for the H_2 case. In contrast, the effectively promoted NO_2 reduction to NO by C_3H_6 or CO creates a mixture of fast and slow SCR feed conditions at low temperatures. The organic intermediates formed from the reaction between C_3H_6 and NO_2 somewhat offset the benefits of the additional fast SCR pathway, decreasing the NO_x conversion relative to that observed for the CO case. At temperatures exceeding 270 °C, C_3H_6 has an increasingly negative effect due to the increasing extent of the standard SCR pathway, while CO again has a slightly negative effect in terms of NO_x conversion. This is similar to the trend for fast SCR reaction. The same explanation for the effects of CO and C_3H_6 on the fast SCR reaction can be applied for the slow SCR reaction. This will be discussed next based on step-response experiments.

3.3.2 Step-response method

A step-response was employed to examine both the transient and steady state behaviors to further elucidate the effects of C_3H_6 and CO on the NH_3 -SCR reaction mechanism. The five-phase protocol depicted in Figs. 10 and 11 included slow SCR reactions (500 ppm NO_2 + 500 ppm NH_3 ; Phase 1), addition of the reducing agent (500 ppm C_3H_6 or 1% CO) to the slow SCR feed in the absence (Phase 2) or presence (Phase 3) of 5% O_2 ,

followed by the reaction of these reductants with NO_2 in the absence of NH_3 with O_2 present (Phase 4) or absent (Phase 5).

Fig. 10 describes the evolution of the effluent concentrations of NO , NO_2 , C_3H_6 , N_2O and NH_3 , during the five-phase protocol at 400°C . A sudden increase in NO concentration occurs upon the introduction of C_3H_6 in Phase 2. This is followed by a slow decrease of the NO concentration, approaching a new steady state after an extended C_3H_6 exposure. The sharp increase in NO concentration suggests an active C_3H_6 -assisted NO_2 conversion to NO (R3). Along with increased NO concentration, the NH_3 concentration increases at a somewhat slower rate presumably due to its continued adsorption on the downstream catalyst. The NH_3 concentration stabilizes at twice the NO steady-state concentration. This confirms that in addition to the NH_3 -SCR pathway, a fraction of the NO_x is reduced via HC-SCR. Subsequent O_2 introduction in Phase 3, leads to a sharp drop in both NH_3 and NO concentrations to the same lower level, indicating that the standard SCR pathway is the primary pathway for NO_x reduction based on the 1:1 $\text{NO}_x:\text{NH}_3$ stoichiometry. The results confirm that lack of O_2 during Phase 2 hinders the standard SCR reaction and thus limits the NO_x reduction. There is a minor performance loss relative to Phase 1 due to the poisoning by oxidation intermediates. Switching off NH_3 in Phase 4 increases the NO concentration and decreases the C_3H_6 concentration. HC-SCR is less effective for NO_x reduction than NH_3 -SCR, and only achieves about 50% NO_x conversion. Further removal of oxygen during Phase 5 confirms that the activity of HC-SCR depends on the oxygen content, which promotes formation of oxygenates and their reaction with NO , as discussed in Sec. 3.1.

Fig. 11 shows the effluent NO , NO_2 , CO , N_2O , and NH_3 concentrations following the five-phase protocol at 400°C . Compared to the significant jump in NO output upon C_3H_6 introduction in Fig. 10, a slight increase in NO concentration (less than 20 ppm) occurs following CO addition. This indicates that the interaction mechanisms of CO and C_3H_6 with NO_x are different. The proposed CO -assisted nitrate reduction to nitrite enables a fast SCR pathway (R15) to prevail in Phase 2, relative to the slow SCR dominant in the prior phase or the standard SCR dominant in Phase 2 of Fig. 10. The slightly increased NO concentration coincides with the prevailing of surface nitrites due to CO , some of

which react with NO_2 to form NO (R8). Adding O_2 during Phase 3 causes both NH_3 and NO to vanish due to their oxidation. Turning off NH_3 during Phase 4 sharply increases NO concentration, proving that CO is less effective in NO_x reduction than either NH_3 -SCR or HC -SCR. Subsequent O_2 removal in phase 5 has negligible effect on either NO or NO_2 profiles, suggesting that O_2 does not affect NO_2 reduction by CO .

3.3.3 N_2O formation

The recently US EPA 2017-25 greenhouse gas regulation capped the N_2O emission from LD and HD vehicles [1]. A concern regarding SCR reaction with a high feed NO_2/NO_x ratio is the relatively high N_2O emission at low temperatures due to decomposition of ammonium nitrates ($\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}$) above 200°C [39]. Figs 10 and 11 show that the trace amount of N_2O vanishes following either the C_3H_6 or CO induction period in Phase 2. This led us to examine N_2O emission during the slow SCR reaction under temperature ramp experiments in Sec. 3.3.1. Less N_2O was emitted when either C_3H_6 , CO or H_2 was present with C_3H_6 resulting in the lowest N_2O emission (data not shown).

Ammonium nitrates are commonly considered the main source of N_2O production. Temperature-programmed desorption (TPD) of pre-loaded NH_4NO_3 in the presence of CO or H_2 or C_3H_6 was conducted as shown in Fig. 12. As described in the Experimental Section, the clean catalyst was initially loaded with an equal amount of ammonium nitrates by exposing the catalyst to NO_2 and NH_3 for 30 mins at 200°C . After flushing with Ar , a TPD at $15^\circ\text{C}/\text{min}$ rate was followed either without or with one of the three reducing agents in the carrier gas. For the baseline sample, a peak N_2O desorption is observed at about 320°C . Note that only a trace amount of NO_2 is recorded (data not shown), confirming the high selectivity of NH_4NO_3 for decomposition to N_2O . N_2O production is greatly reduced relative to the baseline when either C_3H_6 , CO or H_2 is present. Table. 2 describes the reduced N_2O release in the presence of each reductant. This suggests the consumption of surface NH_4NO_3 by these reductants, which otherwise could decompose to N_2O at elevated temperature. It is likely that each reductant is capable of reducing NH_4NO_3 to NH_4NO_2 which can readily decompose to N_2 instead of N_2O .

3.4 Impact of CO, H₂ and C₃H₆ on cyclic NH₃-SCR reduction

The SCR unit in a LNT-SCR configuration is periodically exposed to lean and rich environments. Thus, it is necessary to study the effect of intermittent rich exposure on NH₃-SCR behavior. Lean/rich cycling experiments (baseline) were performed as reported in Table 1. These included the 5s exposure to a rich phase of 500 ppm NH₃ and 300 ppm NO_x, followed by 30s exposure to a lean phase of 300 ppm NO_x + 5% O₂ in a carrier gas. Reducing agents (1% CO + 1% H₂ or 500 ppm C₃H₆) were introduced in the rich phase with NH₃ for comparison.

Fig. 13 compares the effects of CO + H₂ and C₃H₆ in the rich phase on the cycle-averaged NO_x conversion. To simplify the study, we have combined the addition of CO with H₂. Contrary to the steady-state operation for which a negative effect of C₃H₆ was encountered on almost all NH₃-SCR reactions, except for the low-temperature region of slow SCR reaction, C₃H₆ has a significantly positive impact under cyclic conditions. In a previous paper [40], we reported that cyclic operation can help mitigate the C₃H₆ poisoning effect due to the removal of organic intermediates through their reaction with NO_x and/or O₂ during the lean phase. This purge contributes to additional NO_x reduction via HC-SCR pathway. Both mitigated C₃H₆ poisoning and additional HC-SCR contribution enhanced NO_x conversion under cyclic condition. This is consistent with the report by Kim et al. of the additive contribution of C₃H₆ and NH₃ to cycle-averaged NO_x reduction during the standard SCR reaction [21]. CO + H₂ addition enhances the NO_x conversion but to lower extent for both fast and slow SCR.

Fig. 14 shows the periodic temporal effluent concentrations of NO_x, NO, NO₂ for standard and slow SCR reactions at 350 °C. The total NO_x (NO + NO₂) concentration profiles in one cycle are shown in the left half of the figures, while the right half describes the individual NO and NO₂ profiles. No NH₃ slip happens in any of the cases. Fig. 14a shows that the addition of CO + H₂ during standard SCR reaction has a very minor effect on all baseline NO_x, NO and NO₂ profiles. This is expected because, as shown in Fig. 1, CO and H₂ do not react with NO + O₂. In contrast, C₃H₆ introduction affects the NO_x transient behavior. For the baseline case, the NO_x concentration peaks at the end of the lean phase and drops to its lowest level at the onset of the lean phase. It

then gradually increases due to the depletion of stored NH_3 . In contrast, when C_3H_6 is fed, the NO_x concentration peaks at the end of rich phase and then gradually decreases and stabilizes during the lean phase. The accumulation of propene itself or its oxidized intermediates during the rich feed inhibits the NH_3 -SCR pathway. NO_x reduction by NH_3 is retarded and this leads to a delayed appearance of NO_x peak at the end of rich phase. The removal of those intermediates by NO_x and O_2 during the early stage of the lean phase enables the HC-SCR and NH_3 -SCR reactions to gradually decrease the NO_x slip.

For the slow SCR conditions in Fig. 14b, all three cases exhibit similar transient NO_x concentration. The smallest NO_x slip occurs for C_3H_6 , followed by $\text{CO} + \text{H}_2$ feed and the baseline case. The higher reactivity of C_3H_6 with NO_2 than that with $\text{NO} + \text{O}_2$, leads to smaller amounts of surface intermediates blocking the active sites. Thus, a high NO_2/NO_x ratio can help to alleviate C_3H_6 poisoning and thus enable both the HC-SCR and NH_3 -SCR pathways to proceed without interfering with each another. The lower NO_x slip for the $\text{CO} + \text{H}_2$ case, is consistent with their capability to convert NO_2 to N_2 (Fig. 2). The temporal NO and NO_2 profiles reveal that only NO_2 breakthrough occurs for the baseline case over the entire cycle, while considerable NO slip occurs for both C_3H_6 and $\text{CO} + \text{H}_2$ cases. For C_3H_6 feed case, C_3H_6 and its derivatives stored during the rich feed, continue to promote NO_2 reduction in the ensuing lean feed. For $\text{CO} + \text{H}_2$ feed case, since their adsorption on this catalyst is negligible (data not shown), the high amount of surface nitrites formed from nitrates reduction by CO and H_2 during the rich feed is the main cause for the NO production (R8) in the lean phase.

4. Conclusions

We investigated the roles of CO , H_2 and C_3H_6 reductants in reactions with NO_x , NH_3 storage and oxidation, as well as in NH_3 -SCR reactions over a commercial Cu-chabazite SCR catalyst. The main findings are:

- C_3H_6 , CO and H_2 promote NO_2 reduction to NO to different extents by distinct pathways. C_3H_6 -assisted NO_2 decomposition is the most effective, occurring via organic intermediates. CO reduces nitrates to nitrites that then rapidly react with NO_2 to produce NO . H_2 follows the same nitrate-related pathway as CO for NO_2 reduction

but is less effective. H_2 can also reduce Cu cations to metallic Cu that catalyzes H_2 -SCR of NO_x to N_2 and NH_3 at high temperatures and under anaerobic condition.

- For NO_2 reaction with H_2 , high oxygen levels and low temperatures favor the nitrate-related NO_2 reduction pathway. The opposite trend drives reduction pathway towards H_2 -SCR.
- C_3H_6 affects NH_3 -SCR reactions mainly by its interaction with NO_2 . Its main role is to compete with NH_3 for adsorbed NO_2 to produce oxygenates, and release NO. Thus, an increasing NO/ NO_x ratio changes the dominant NH_3 -SCR pathway. For example, contingent on the temperature range, a slow SCR reaction can be changed to either a fast or a standard SCR condition.
- CO competes with NO for nitrates decomposition to nitrites, leading to a negligible impact on standard and fast SCR pathways but a positive effect on slow SCR reaction.
- During lean/rich cycling, C_3H_6 addition in the rich phase has a significantly positive effect, increasing cycle-averaged NO_x conversion over the entire temperature range. Both high NO_2/NO_x ratio and sufficiently long lean-phase purge can greatly mitigate propene poisoning, enabling an additive contribution of both HC- and NH_3 -SCR pathways. CO and H_2 also enhance the cycle-averaged NO_x conversion but to a smaller extent.
- All three reductants can limit N_2O production during the slow SCR reaction. This is attributed both to the inhibition of NH_4NO_3 formation or the promotion of NH_4NO_3 consumption.
- Under the conditions used in this study, the individual reducing agents do not compete with NH_3 for storage sites. Propylene inhibits NH_3 oxidation primarily due to oxidation intermediates that block active sites, while CO and H_2 have almost no impact on NH_3 oxidation.

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6. Reference

- [1] T. Johnson, SAE Int. J. Engines 6 (2013) 699-715.
- [2] G.D. Neely, J.V. Sarlashkar, D. Mehta, SAE Int. J. Engines 6 (2013) 1009-1020.
- [3] M.P. Harold, Current Opinion in Chemical Engineering 1 (2012) 303-311.
- [4] L. Xu, R. McCabe, P. Tennison, H.-W. Jen, SAE Int. J. Engines 4 (2011) 158-174.
- [5] Y. Matsuo, S. Ishimaru, M. Amano, N. Komatsu, S. Aoyagi, H. Dan, T. Endo, Y. Matsuzono, T. Ito, M. Nagata, SAE Technical Paper 2013-01-0536 (2013).
- [6] Y. Liu, Y. Zheng, M.P. Harold, D. Luss, Applied Catalysis B: Environmental 132-133 (2013) 293-303.
- [7] Y. Zheng, Y. Liu, M.P. Harold, D. Luss, Applied Catalysis B: Environmental 148 (2014) 311-321.
- [8] G.D. Neely, D. Mehta, J. Sarlashkar, SAE Technical Paper 2014-01-1552 (2014).
- [9] J. Jeon, H. Seo, K. Lee, S. Kwon, K. Bae, SAE Technical Paper 2014-01-152 (2014).
- [10] T. Johnson, SAE Technical Paper 2014-01-1491 (2014).
- [11] J.E. Parks, V. Prikhodko, W. Partridge, J.-S. Choi, K. Norman, S. Huff, P. Chambon, SAE Int. J. Fuels Lubr. 3 (2010) 956-962.
- [12] R.D. Clayton, M.P. Harold, V. Balakotaiah, Applied Catalysis B: Environmental 81 (2008) 161-181.
- [13] G. Cavataio, J.R. Warner, J.W. Girard, J. Ura, D. Dobson, C.K. Lambert, SAE Int. J. Fuels Lubr. 2 (2009) 342-368.
- [14] Y. Huang, Y. Cheng, C. Lambert, SAE Int. J. Fuels Lubr. 1 (2009) 466-470.
- [15] A. Kumar, K. Kamasamudram, A. Yezerets, SAE Int. J. Engines 6 (2013) 680-687.
- [16] J. Girard, R. Snow, G. Cavataio, C. Lambert, SAE Technical Paper 2008-01-0767 (2008).
- [17] C. He, Y. Wang, Y. Cheng, C.K. Lambert, R.T. Yang, Applied Catalysis A: General 368 (2009) 121-126.
- [18] I. Heo, Y. Lee, I.-S. Nam, J.W. Choung, J.-H. Lee, H.-J. Kim, Microporous and Mesoporous Materials 141 (2011) 8-15.
- [19] J.-Y. Luo, A. Yezerets, C. Henry, H. Hess, K. Kamasamudram, H.-Y. Chen, W.S. Epling, SAE Technical Paper 2012-01-1096 (2012).

- [20] J. Wang, Y. Ji, Z. He, M. Crocker, M. Dearth, R.W. McCabe, *Applied Catalysis B: Environmental* 111-112 (2012) 562-570.
- [21] M.-Y. Kim, J.-S. Choi, M. Crocker, *Catalysis Today* 231 (2014) 90-98.
- [22] M.A. Smith, C. Depcik, J. Hoard, S. Bohac, D. Assanis, *SAE Technical Paper* 2013-01-1062 (2013).
- [23] P. Namkhang, P. Kongkachuichay, *Journal of Nanoscience and Nanotechnology* 15 (2015) 5410–5417.
- [24] F. Gao, E. Walter, E. Karp, J. Luo, R. Tonkyn, J.H. Kwak, J. Szanyi, C.H.F. Peden, *Journal of Catalysis* 300 (2013) 20-29.
- [25] O. Gorce, F. Baudin, C. Thomas, P. Da Costa, G. Djéga-Mariadassou, *Applied Catalysis B: Environmental* 54 (2004) 69-84.
- [26] P. Forzatti, L. Lietti, I. Nova, S. Morandi, F. Prinetto, G. Ghiotti, *Journal of Catalysis* 274 (2010) 163-175.
- [27] P. G. Savva, C. N. Costa, *Catalysis Reviews: Science and Engineering* 53 (2011) 91-151.
- [28] J. Xue, X. Wang, G. Qi, J. Wang, M. Shen, W. Li, *Journal of Catalysis* 297 (2013) 56-64.
- [29] I. Lezcano-Gonzalez, U. Deka, B. Arstad, A. Van Yperen-De Deyne, K. Hemelsoet, M. Waroquier, V. Van Speybroeck, B.M. Weckhuysen, A.M. Beale, *Physical Chemistry Chemical Physics* 16 (2014) 1639-1650.
- [30] F. Gao, J. H. Kwak, J. Szanyi, C.H.F. Peden, *Top Catal* 56 (2013) 1441–1459
- [31] R. Raj, M.P. Harold, V. Balakotaiah, *Industrial & Engineering Chemistry Research* 52 (2013) 15455-15465.
- [32] D. Wang, L. Zhang, K. Kamasamudram, W.S. Epling, *ACS Catalysis* 3 (2013) 871-881.
- [33] J.Y. Luo, H. Oh, C. Henry, W. Epling, *Applied Catalysis B: Environmental* 123 (2012) 296-305.
- [34] F. Solymosi, T. Bansagi, *Journal of Catalysis* 156 (1995) 75-84
- [35] G. Piazzesi, D. Nicosia, M. Devadas, O. Krocher, M. Elsener, A. Wokaun, *Catalysis Letters*, 115 (2007) 33-39.
- [36] S. Tamm, H.H. Ingelsten, A.E. Palmqvist, *Journal of Catalysis* 255 (2008) 304-312.

- [37] C. Prestipino, L. Capello, F. D'Acapito, C. Lamberti, *Phys. Chem. Chem. Phys.* 7 (2005) 1743-1746.
- [38] A. Grossale, I. Nova, E. Tronconi, D. Chatterjee, M. Weibel, *Journal of Catalysis* 256 (2008) 312-322..
- [39] K. Kamasamudram, C. Henry, N. Currier, A. Yezerets, *SAE Int. J. Engines* 5 (2012) 688-698.
- [40] Y. Zheng, D. Luss, M.P. Harold, *SAE Int. J. Engines* 7 (2014) 1280-1289.

Table 1

Gas condition for baseline cycling test		
Gas	Lean (30s)	Rich (5s)
NOx*	300 ppm	300 ppm
NH ₃	—	500 ppm
O ₂	5%	1%
CO ₂	2%	2%
H ₂ O	2.5%	2.5%

* NO/NOx=1 for standard, 0.5 for fast and 0 for slow SCR reactions

Table 2

Accumulated N ₂ O release from TPD of NH ₄ NO ₃ ^a	
Conditions	N ₂ O release, μ mol
Baseline	5120
w/H ₂	3414
w/CO	1062
w/C ₃ H ₆	416

^a NH₄NO₃-preloaded catalyst is heated at 15 °C/min from 200 to 400 °C with or without each reductant (1% CO, 1% H₂, and 500 ppm C₃H₆) in carrier gas of 2.5% H₂O, 2% CO₂ and balance Ar.

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

Fig.7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13

Fig. 14