



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.

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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; NO + NO₂) in a net oxidizing environment. Ever-tightening Tier 3 and LEV III emission regulations exacerbate this technological challenge [2]. Two commercialized deNO_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 N₂ by reaction over vanadium-based or transition metal exchanged zeolite catalysts with NH₃ generated from urea hydrolysis. SCR is the leading deNO_x solution for mid- or heavy-duty vehicles and can achieve over 95% deNO_x efficiency at

practically relevant space velocities. It requires an onboard urea storage and delivery system with a minimum urea dosing temperature requirement of ~200 °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, H₂ 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 N₂O and NH₃.

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 NH₃ 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 °C) due to decreased NO_x storage capacity and NH₃ 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

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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 NH₃ generation by the LNT. This may generate relatively high levels of CO, H₂ 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 NH₃-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 C₃H₆ due to carbon deposits during standard SCR (NO + NH₃ + O₂) over a Fe-beta zeolite [17]. Heo et al. attributed the competitive adsorption of NH₃ and C₃H₆ on the catalyst as well as undesired NH₃ consumption by side reactions to the decreased NH₃-SCR activities of Fe- or Cu-ZSM-5 [18]. Epling et al. compared the effects of C₃H₆ and dodecane (n-C₁₂H₂₆) 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 C₃H₆ 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 h 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 h⁻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

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