



Research Paper

Unified mechanistic model for Standard SCR, Fast SCR, and NO₂ SCR over a copper chabazite catalyst

M. Bendrich^{a,b}, A. Scheuer^b, R.E. Hayes^a, M. Votsmeier^{b,c,*}^a University of Alberta, 116 Street, Edmonton, Alberta, T6G 2V4, Canada^b Umicore AG & Co. KG, Rodenbacher Chaussee 4, 63457 Hanau, Germany^c Technische Universität Darmstadt, Alarich-Weiss-Str. 8, 64287 Darmstadt, Germany

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ABSTRACT

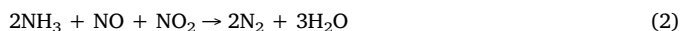
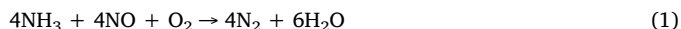
Mechanistic proposals for the different SCR subreactions are integrated into one surface reaction mechanism that describes the main SCR reactions (Standard SCR, Fast SCR, NO₂ SCR), transient effects due to nitrate storage, as well as the production of the side product N₂O over a copper chabazite catalyst. The mechanism is parameterised to steady state and transient experiments, and is shown to predict the behaviour of the catalyst during a driving cycle, without any refitting of kinetic parameters.

A dual site approach is used, where site 1 accounts for the adsorbed ammonia that forms on the Brønsted acid sites and copper ions, while site 2 is a copper ion (Cu²⁺-OH) where nitrites and nitrates are adsorbed. All main SCR reactions proceed *via* a reaction between ammonia and nitrites (ammonium nitrite pathway) to produce nitrogen; nitrites are also the linking species between the Standard SCR and NO oxidation reactions. Reactions between nitrates and ammonia to produce ammonium nitrate are also included, along with ammonium nitrate decomposition pathways (i.e., *via* NO addition to feed). Additionally, a global reaction taking place between adsorbed ammonia and gaseous NO₂ to produce N₂ at low temperatures (< 250 °C) is added, to account for an observed reaction taking place on the copper-free zeolite.

The mechanism was used to analyse the importance of nitrate formation during a standard driving cycle. Surprisingly, although a significant amount of inhibitive ammonium nitrate is modelled to form during low temperature Fast and NO₂ SCR steady state experiments, almost no ammonium nitrate is predicted to form during the driving cycle, thus allowing for a higher reaction activity than predicted based on steady state data. From a modelling and catalyst testing perspective, this shows the importance of capturing the catalyst's transient behaviour rather than only steady state conditions, since steady state is not necessarily reached during practical driving scenarios.

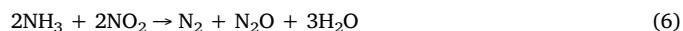
1. Introduction

Selective catalytic reduction (SCR) is used in the automotive industry to reduce NO_x gases. In the SCR process, ammonia, the reducing agent, is generated onboard through the hydrolysis of urea. The ratio of NO to NO₂ in the exhaust gas entering the SCR catalytic converter affects the selectivity of the main reactions, which are Standard SCR (1), Fast SCR (2), and NO₂ SCR (3) [1,2].



Side reactions such as ammonia oxidation (4) and NO oxidation/

NO₂ decomposition (5) at high temperatures (i.e., > 400 °C) [3,4], or ammonium nitrate formation at low temperatures (i.e., < 200 °C), leading to N₂O formation [5,6], can also occur.



Several catalysts have been used for the automotive SCR. Vanadium catalysts were first implemented because of their use in stationary deNO_x applications [7], however, Fe- and Cu-zeolite catalysts became a popular choice owing to requirements for a higher activity at low temperatures and a greater stability at higher temperatures [3]. Recently, catalysts based on copper chabazite (CHA) structures have been

* Corresponding author at: Umicore AG & Co. KG, Rodenbacher Chaussee 4, 63457 Hanau, Germany.
E-mail address: martin.votsmeier@eu.umicore.com (M. Votsmeier).

commercialized, which have a smaller pore-structure compared to Cu-ZSM-5 and Cu-BEA [8].

As a result, there has been a significant amount of research published on Cu-CHA catalysts, which led to the identification of possible active sites and the development of mechanisms for the different reactions [9]. The purpose of the current work is to integrate this existing knowledge into a comprehensive model that captures the different subreactions as well as transient effects due to nitrate storage.

In terms of research on the active sites, it has been proposed that Cu^{2+} is found in the CHA's 6-membered ring and at higher loadings, Cu species can be found in some form of Cu_xO_y in the 8-membered ring [10–12]. Both the copper sites and Brønsted acid sites are responsible for ammonia adsorption, but ammonia stored on copper is significantly more reactive in SCR [13,14], whereas the Brønsted sites mainly act as ammonia storage sites [11].

Various mechanistic pathways have been proposed to describe the main SCR reactions (1, 2, 3). While it was originally believed that the oxidation of NO to NO_2 (5) is the rate limiting step that connects Standard SCR (1) to Fast SCR (2) [15], evidence by Ruggeri et al. points to nitrite-like species being the linking intermediate between NO oxidation and Standard SCR over zeolites [16–18]. Kwak et al. also proposed that NO^+ and not NO_2 is an intermediate over a chabazite catalyst, and presented a catalytic cycle for Standard SCR where NO is responsible for the reduction of Cu^{2+} , and oxygen is responsible for the re-oxidation [19]. Several catalytic cycles have been proposed for Standard SCR only [20–22] or Standard and Fast SCR [23] over Cu-CHA. NO_2 SCR is not captured by these proposed cycles. Nevertheless, there have been separate mechanisms proposed to describe Fast SCR [24,25] and NO_2 SCR [26] on Fe-zeolite catalysts.

Fewer papers have focused on the simulation of SCR over Cu-CHA catalysts. A global Cu-CHA model by Olsson et al. [27] used three active sites to predict the behaviour of ammonia adsorption, ammonia oxidation, Standard SCR to N_2 , and Standard SCR to N_2O ; the study focused on NH_3 -NO feeds, thus no NO_2 was included. To compare Cu-CHA to Fe-ZSM-5 and combined Fe- and Cu- catalysts, Metkar et al. [28], implemented a global, single site model for Cu-CHA that could predict the steady state conversions for different NO_2/NO_x ratios. One active site was used for ammonia adsorption. The model could simulate the steady state conversions for ammonia oxidation to N_2 , NO oxidation, Standard SCR to N_2 , Fast SCR to N_2 , NO_2 SCR to N_2 , and NO_2 SCR to N_2O , with ammonium nitrate gas species as an intermediate.

The formation of nitrates and nitrites may lead to additional transient effects that are not captured in models that use ammonia as the only stored species [6]. For instance, ammonium nitrate formation leads to significant low temperature dynamics. This issue is particularly important for Cu-CHA, since owing to the smaller pore size, ammonium nitrate is more stable on Cu-CHA compared to its larger-pore counterparts (i.e., Cu-BEA) [5]. In this work, we integrated mechanistic information and pathways published in the literature to develop a surface reaction mechanism that captures the transients related to mixed NH_3 -NO/ NO_2 feeds for Cu-CHA. The mechanism relies on a dual site approach, where one active site is responsible for ammonia adsorption, while the other accounts for the formation of nitrites and nitrates. The kinetic parameters of the reactions were fit to steady state and transient experiments, and model Standard SCR, Fast SCR, and NO_2 SCR conditions as well as side reactions such as ammonia oxidation and ammonium nitrate formation, storage, and decomposition. In a final step, the model is used to simulate a driving cycle without refitting of the kinetic parameters. Comparison of the simulated surface species formed during the driving cycle versus steady state experiments indicates that the steady state conditions are not reached during the driving cycle, and emphasizes the importance of modelling transients rather than only steady state activity.

2. Methods

2.1. Laboratory reactor measurements

The experiments were completed with a commercial, state-of-the-art, copper chabazite catalyst with a commercial copper loading supported on a cordierite substrate. The monolith samples had the following properties: 2.5 cm diameter, 5.1 cm length, cell density of 400 cpsi, and a wall thickness of 109 μm . The samples were aged in a flow of 10% O_2 and 10% H_2O with N_2 as the balance gas for 16 h at 750 °C. Additionally, a Cu-free, zeolite catalyst sample was used. This sample had 78% of the zeolite content of the Cu-CHA sample, and it was aged for 16 h at 700 °C.

The monolith sample was placed inside a quartz tube through which the feed gas of selected composition and temperature was passed. A thermocouple monitored the inlet gas temperature, which was recorded and is used throughout this paper; outlet temperatures were not recorded, however investigations on the experimental set-up show a maximum temperature difference of 4 °C. The outlet gas composition was measured by an FTIR. The tubing from the reactor to the FTIR was heated to 185 °C to avoid ammonium nitrate deposition.

Three experiment types were used: steady state, transient temperature programmed desorption (TPD), and temperature programmed surface reaction (TPSR). All experiments had 5% H_2O and 6% O_2 , with N_2 as the balance gas, and began with a pre-treatment to ensure that no species were adsorbed on the catalyst. Likewise, the gas hourly space velocity (GHSV) for all experiments was 50,000 h^{-1} at STP, with the exception of the Fast SCR experiments being completed at 125,000 h^{-1} at STP.

For the steady state experiments, the gas of desired composition and temperature was passed over the monolith until steady state was reached, at which point the steady state outlet composition and temperature were recorded. To capture the transient dynamics, TPD experiments were used to determine the ammonia and NO_2 adsorption/desorption properties. In this experiment, the desired species were added at a given temperature. As the species were adsorbed by the catalyst, a dead-time was first exhibited, followed by a rapid increase in the outlet concentration after the active sites have been filled. Once the outlet concentration had reached steady state, the species were no longer added to the feed, allowing for any desorption of loosely bound species. A temperature ramp followed, allowing for the desorption of the remaining species. The transient TPSR experiments were similar to the TPD experiments, only multiple species were added in various orders, to allow for a reaction between desired species.

2.2. Engine test bench measurement

A WHTC driving cycle was performed on an engine test bench using a Cu-CHA catalyst. The Cu-CHA monolith used at the engine test bench had the following properties: 24.1 cm diameter, 34.3 cm length, cell density of 400 cpsi, and a wall thickness of 74 μm . The catalytic converter was aged in 10% O_2 and 10% H_2O , with N_2 as the balance gas for 16 h at 750 °C.

The engine test bench catalytic converter system consisted of a diesel oxidation catalyst (DOC), a diesel particle filter (DPF), and the SCR catalyst. There was no ammonia initially stored on the SCR catalyst. The aqueous urea solution was injected between the DPF and SCR based on an NH_3/NO_x constant dosing strategy ratio of 1.2. No urea dosing restriction was in place since the temperature of the WHTC driving cycle, which started at an initial temperature of 200 °C rather than a cold start, was always above 180 °C. An FTIR, CLD, and oxygen sensor measured the outlet composition.

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