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Modeling and Optimization of Multi-Functional Ammonia Slip Catalysts for Diesel Exhaust Aftertreatment

Thomas Klint Torp^{a,b}, Brian Brun Hansen^b, Peter N.R. Vennestrøm^c, Ton V.W. Janssens^c, and Anker Degn Jensen^{b*}

^a Haldor Topsøe A/S, Haldor Topsøe Allé 1, 2800 Kgs. Lyngby, Denmark

^b Department of Chemical and Biochemical Engineering, Technical University of Denmark, Søtofts Plads 229, 2800 Kgs. Lyngby, Denmark

^c Umicore Denmark A/S, Kogle Alle 1, 2970 Hørsholm, Denmark

*Correspondence to aj@kt.dtu.dk

Abstract

Ammonia slip catalysts (ASC) are used downstream of the NH_3 -selective catalytic NO_x reduction (SCR) system, to minimize ammonia slip from transport sector SCR units. The ASC may consist of an SCR active layer for NO_x control, a layer with oxidation functionality for ammonia conversion, or a combination thereof, either as individual layers or as a single mixed layer. Mathematical models of such systems involve flow and mass transfer in the monolithic channels as well as coupled reaction/diffusion processes in the catalytic layers. In this work, we develop a single channel 1D-1D (pseudo 2D) steady-state tank-in-series mathematical model for monolithic ammonia slip catalysts with up to two layers. Kinetics of relevant reactions over the Cu-Beta zeolite and the Pt/TiO_2 layer, including SCR, ammonia oxidation and the formation of N_2O , were derived based on an extensive flow reactor study. The model was validated based on experiments using four different small-scale ASC monoliths, showing good agreement between the model predictions and the experimental results. Comparison of ten ASC configurations for the oxidation of 200 ppm NH_3 at 300°C , show that configurations with a pure layer of NH_3 oxidation catalyst, generate undesirable high N_2O and NO_x levels. The best ASC configurations feature fast diffusion in the catalytic layers (a high effective diffusion coefficient), a thin top layer loading with some ammonia oxidation catalyst, and a mixed layer of ammonia oxidation catalyst and the SCR catalyst to limit the formation of N_2O and NO_x .

Keywords

Ammonia Slip Catalyst, SCR, Ammonia Oxidation, Modeling, Diesel Exhaust Aftertreatment, Multi-objective Optimization

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1. Introduction

Nitrogen oxides (NO_x) are harmful for human health and the environment, and therefore, the emission of NO_x from diesel engines is strictly regulated in many places [1–3]. To mitigate NO_x emissions from diesel engines, the exhaust aftertreatment system contains a catalyst to convert NO_x to nitrogen and water. This conversion is based on the selective catalytic reduction (SCR) by NH_3 , and urea is added to the exhaust gas as a source of NH_3 [3]. In practice, a small excess of urea is used to improve the NO_x reduction, but this also results in a slip of NH_3 from the SCR catalyst [4]. Therefore, an ammonia slip catalyst (ASC) is placed immediately after the SCR catalyst, to limit unwanted emissions of NH_3 .

Ideally, an ammonia slip catalyst oxidizes the NH_3 with O_2 to nitrogen and water. These catalysts are usually based on supported Pt particles, which are very active for the oxidation of NH_3 by O_2 , already at around 200°C [3, 5, 6]. However, at higher temperatures, Pt based catalysts are not very selective for N_2 , and produce considerable amounts of N_2O between $225\text{--}300^\circ\text{C}$, and NO_x at temperatures above 250°C [3, 6–14]. The formation of NO_x and N_2O in an ASC is counterproductive for abatement of NO_x . Furthermore, the formation of N_2O is problematic since N_2O is a strong greenhouse gas, about 300 times more potent than CO_2 [3], and emissions of N_2O are likely to be restricted in future emission regulations as well.

To improve the selectivity for N_2 , an ASC usually consists of an ammonia oxidation (AMOX) catalyst component, often based on Pt, combined with an SCR catalyst [3, 6–15]. The SCR catalyst effectively converts the NO_x produced from oxidation of NH_3 to N_2 , as long as NH_3 is present, via the NH_3 -SCR reactions. There are several ways to combine the AMOX component with an SCR catalyst, leading to different configurations of the ASC. The simplest way is to mix the SCR catalyst with the AMOX catalyst [8, 10–12, 14, 15]. Often, however, the SCR catalyst is applied as a separate layer on top of the AMOX catalyst, creating a dual layer structure [3, 6–12, 14, 16], or as a hybrid consisting of a mixed bottom layer with an SCR top layer [10, 14]. In general, adding an SCR component to the ASC improves the N_2 selectivity compared to that of a Pt based AMOX catalyst alone.

The SCR catalyst that is used in an ASC must be very active for SCR, in order to obtain sufficient N_2 selectivity. Therefore, Cu- or Fe-zeolites are used in ASC, because these are the most active catalysts available for SCR. Mathematical modeling and experimental studies of ASC with Pt/ Al_2O_3 and Cu- or Fe-zeolite components have demonstrated a number of advantages and disadvantages of the different designs of the ASC [5–7, 10–12, 14, 15, 17, 18]. In general, there is a trade-off between NH_3 conversion and N_2 selectivity. A single mixed layer design provides the highest accessibility of the gas species to the AMOX catalyst, leading to a higher NH_3 conversion, but also a lower selectivity for N_2 , albeit with the advantage of a lower N_2O selectivity, as compared to a Pt catalyst only [8, 10–12, 14, 15]. A dual layer design with an SCR catalyst on top of the AMOX catalyst enhances the N_2 selectivity, but lowers the NH_3 conversion, since the SCR catalyst layer introduces a mass transfer resistance to the AMOX catalyst [8, 10–12, 14, 15]. The mass transfer can be improved by adding starch to the washcoat formulation, which after calcination leaves additional porosity [16]. A hybrid configuration consisting of an SCR top layer and a mixed bottom layer leads to an intermediate NH_3 conversion and product selectivity [8, 10–12, 14, 15].

Most studies that compare the performance of different configurations for the ASC [5–12, 14, 15, 17, 19, 20] are limited to combinations of given amounts of AMOX and SCR components, which are then distributed in different ways according to preselected catalyst configurations. In some studies, the basic configuration is kept constant and the amount of a catalyst component is varied, for example, the amount of Pt catalyst in the mixed layer in a hybrid catalyst design (top Cu/SSZ-13, base Pt/ Al_2O_3

+ Cu/SSZ-13) [14]. However, the optimal performance of an ASC depends both on the amounts of SCR and AMOX components, and on the configuration of the catalyst. A non-optimal formulation will not reveal the full potential of a given ASC configuration, and consequently, a comparison of catalysts with different formulations can lead to misleading conclusions, if the possible effects of the configuration are ignored.

The optimization of an ASC is a multi-objective optimization problem, due to the trade-offs between NH_3 conversion and product selectivity. This means that an optimal ASC design also depends on the requirements for a specific application. For example, in some cases it could be advantageous to focus on low NO_x or N_2O formation in the ASC, rather than maximizing NH_3 conversion, or a high SCR activity in order to effectively extend the upstream SCR unit. Combined, these considerations make it difficult to draw general conclusions on the advantages and disadvantages of the different ASC designs, and they must instead be evaluated case-by-case.

To be able to select a good configuration of an ASC, a good understanding of the interplay of the amounts of the AMOX and SCR catalyst components and the design of the catalyst is necessary. It is therefore desirable to have a model that can translate the process requirements into a suitable configuration of an ASC and guide the development process. In this work, we derive a mathematical model for a single channel of a monolithic ASC and use it to evaluate ten different ammonia slip catalyst configurations through multi-objective optimization. The kinetics of the relevant reactions over Pt-based AMOX and SCR catalyst components, including N_2O formation, are determined based on extensive flow reactor experiments. Furthermore, we use NH_3 oxidation at an intermediate operating temperature of 300°C , relevant for many test cycles, for the evaluation of different catalyst configurations. For each configuration, we consider the amounts of AMOX or SCR catalyst in each layer, the effective diffusion coefficient in the catalyst layers, which is affected by the average pore diameter in the layers, and the intrinsic activity of the AMOX catalyst, which depends on the Pt content in the AMOX catalyst that is added. The optimization results form a set of optimal solutions (Pareto set), which are visualized by Pareto fronts generated for optimization of an ASC configuration. These data are then used to compare and evaluate the potential of different catalyst configurations and formulations. The multi-objective optimization also gives an indication of the sensitivity of the ASC performance to catalyst architecture and is an example of how an optimal ASC can be designed.

2. Experimental

2.1 Catalyst Preparation

2.1.1 Powder Catalysts

The monolithic ASC samples studied in this work were based on the combination of a 1 wt.% Pt on TiO_2 support as the AMOX catalyst, and a 3.5 wt.% Cu-Beta SCR catalyst. The 1 wt.% Pt/ TiO_2 AMOX catalyst was prepared by impregnation of the support material with $\text{Pt}(\text{NH}_3)_4(\text{HCO}_3)_2$ followed by drying at 100°C , and calcination at 550°C in air for 2 hours. The 3.5 wt.% Cu-Beta SCR catalyst was prepared by impregnation of the parent Beta zeolite ($\text{Si}/\text{Al}=20$) with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, followed by drying at 115°C and calcination in air at 550°C . The catalysts were tableted, crushed, and sieved to a fraction of either $106\text{--}150\text{ }\mu\text{m}$ or $150\text{--}300\text{ }\mu\text{m}$ prior to activity measurements using fixed bed reactors.

2.1.2 Monolith Catalysts

Four monolithic ammonia slip catalysts with different configurations were prepared: single layer AMOX, single layer SCR, single mixed layer, and dual layer with the SCR catalyst on top of the AMOX

catalyst layer. The catalysts were prepared by dip coating square channel cordierite monolith substrates with 300 cpsi in slurries of 1 wt.% Pt/TiO₂ (AMOX catalyst) and/or 3.5 wt.% Cu-Beta (SCR catalyst). The aqueous slurries consisted of the respective catalysts and a colloidal silica binder. The slurries were milled to break agglomerates and obtain small catalyst particles with an average catalyst particle size of 3 µm for the AMOX catalyst and 18 µm for the SCR catalyst.

For the SCR catalyst slurry applied to the single layer SCR and the dual layer sample, an aqueous solution of an organic stabilizer (xanthan gum) was added after milling. In order to control the catalyst loading applied by dip coating, the dry matter content was adjusted by adding demineralized water.

In the case of the AMOX catalyst slurry for single layer AMOX and the dual layer sample, Pt-free TiO₂ support material was added in order to dilute the Pt content from 1 wt.% to 0.25 wt.%. The Pt content of a calcined sample of the AMOX catalyst slurry was 0.235 wt.% Pt, as determined by inductively coupled plasma optical emission spectrometry. An aqueous NH₃ solution (30-33 wt.% NH₃) was used to regulate the pH of the washcoat slurry to 9–10.

To avoid differences in the AMOX catalyst loading for the single layer AMOX and dual layer sample, a large monolith substrate (*d* 0.266 m x *L* 0.152 m) with 300 cells per square inch and 6 mil (152 µm) thick channel walls was initially coated with the AMOX washcoat slurry by dip coating. The excess slurry was removed by blowing a stream of air through the channels using an air knife. The coated monolith substrate was then dried overnight at room temperature, with a flow of air through the channels, followed by further drying overnight in an oven at 80°C, and the dried AMOX catalyst coated monolith was cut into smaller samples (*d* 0.05 m x *L* 0.037 m). To prepare the dual layer sample, one of these samples coated with AMOX catalyst was dip coated with SCR washcoat slurry.

The single layer Cu-Beta SCR sample was prepared by dip coating a small (*d* 0.05 m x *L* 0.037 m) sample of uncoated cordierite monolith substrate of the same type used for the initial AMOX catalyst washcoating. The single mixed layer catalyst was prepared using a similar procedure, but using a slurry containing a mixture of the AMOX and SCR catalysts.

After dip coating and removal of excess slurry, the small monolithic catalyst samples were dried at room temperature with a flow of air through the channels for 30 minutes. The monolithic catalyst samples were calcined at 550°C for 2 hours. An overview of the prepared catalysts is presented in Table 1.

2.2 Activity Measurements

2.2.1 Fixed Bed Reactor

The catalytic activity of the AMOX and SCR catalysts were evaluated using two different fixed bed reactor setups.

For the AMOX catalyst, the fixed bed reactor setup used a quartz U-tube reactor (*d*_i = 2 mm) loaded with 5 mg of the 1 wt.% Pt/TiO₂ catalyst (150–300 µm), fixed between two plugs of quartz wool. A thermocouple was placed at the position of the catalyst bed on the outside of the reactor giving a temperature representative of the average catalyst temperature. The feed gas consisted of 500 ppm NH₃, 5 vol.% H₂O, 10 vol.% O₂, and balance N₂, with a total flow of 400 NmL/min. An FTIR gas analyzer (Gaset; CX4000) measured the concentrations of NH₃, NO, NO₂, N₂O, and H₂O in the outlet gas. The N₂ concentration was calculated from the N-balance. The catalyst was heated to 550°C at a rate of 20°C/min in the feed gas and held at these conditions for 1 hour. Afterwards, the catalyst was

stepwise cooled to 200°C, with smaller steps taken for temperatures below 300°C. Steady-state measurements were made at each temperature for a duration of 20 minutes.

A second fixed bed reactor setup was used for the catalytic activity measurements of the 3.5 wt.% Cu-Beta SCR catalyst. A quartz U-tube reactor ($d_i = 6$ mm) was loaded with a mixture of 20 mg catalyst (106–150 μm) and 100 mg SiC (150–300 μm), fixed between two plugs of quartz wool. For measurements made below 225°C, a sample of 40 mg catalyst and 200 mg SiC was used instead to obtain sufficient conversion. The gas flowed upwards through the catalyst bed and the temperature was measured with a thermocouple placed inside the reactor at the catalyst bed outlet. The base of the feed gas consisted of 5 vol.% H_2O , 10 vol.% O_2 , and balance N_2 , with a total flow of 1000 NmL/min. Water was added to the gas mixture by bubbling a separate flow of N_2 through water heated to 80°C. Concentrations of approximately 600 ppm NH_3 and 500 ppm NO_x were used to give an NH_3 -to- NO_x molar ratio of 1.2. The NO_2/NO_x ratio in the feed was varied between 0, 0.5, or 1. The investigation of catalytic activity was performed by initially heating the catalyst to 550°C in a standard SCR mixture for 1 hour followed by cooling to 150°C in the same gas mixture. The catalyst was then stepwise heated to the selected temperatures, and the composition of the reactor exit gas was measured for a duration of 1 hour at each temperature, with feed gas measurements made both before and after. The composition of the reactor exit gases was measured using several methods. The concentrations of NH_3 , NO , and NO_2 were measured using a continuous gas analyzer (Limas11-HW; ABB) and the concentration of H_2O was determined using a humidity probe (HC2-IC102; Rotronic). After the gas analyzer, H_2O was condensed from the gas and the concentration of N_2O in the resulting gas was measured using a micro-GC (Varian; CP-490), and corrected for the concentration of water removed. The N_2 concentration was calculated from the N-balance.

2.2.2 Monolith Flow Reactor

The monolith catalysts were tested for NH_3 oxidation in a flow reactor designed for testing small monolith samples (d 0.05 m $\times$ L 0.037 m). Prior to loading the monolithic catalyst, a small hole was drilled in the middle of the outlet end of the monolith, in order to accommodate the thermocouple placed in the center of the sample giving a temperature representative of the average catalyst temperature. The monolith sample was then loaded into a steel reactor tube, with a gas mixing block placed directly upstream. The base of the feed gas was made by mixing flows of air, N_2 , and H_2O . The gas flow was directed through a pre-heater to heat the gas to the selected temperature of the reactor. NH_3 was added to the feed gas immediately before the mixing block. The feed gas used in this study consisted of 200 ppm NH_3 , 4 vol.% H_2O , 12 vol.% O_2 , in N_2 , at a total flow of 18,200 NL/hr. This corresponds to gas hourly space velocity (GHSV) of 250,000 hr^{-1} , based on the total gas flow and the total volume of the monolith catalyst sample. Shortly downstream of the catalyst, an FTIR gas analyzer (Gaset; CX4000) was used to measure the concentration of NH_3 , NO , NO_2 , N_2O , and H_2O . The catalyst sample was initially heated to 550°C in the feed gas and held at these conditions for 1 hour, and then subsequently cooled to 170°C. The feed gas concentration was measured at a reactor temperature of 170°C; at this temperature the ASC is not active. Steady-state measurements were made afterwards by stepwise heating the catalyst to selected temperatures between 200 and 550°C.

3. Mathematical Models and Multi-Objective Optimization

3.1 Monolith Model

A model was developed to describe the monolithic ASC containing two layers. Each of the two layers in the model contains either an SCR functionality, an AMOX functionality or a combination of both, see Figure 1. The model was used to evaluate ten different configurations as illustrated in Figure 2.

The monolith reactor model is based on a single channel of a monolithic ASC. We have used a tank-in-series approach to simulate the flow in the channel, assuming isothermal, isobaric, and steady-state conditions. For each tank in the model, the mass balance is solved, considering the convective gas flow in and out of the tank, as well as the mass transfer to the surface of the catalyst washcoat. The mass balance then becomes:

$$Q \cdot (C_{g,i,k-1} - C_{g,i,k}) = k_{mt,i} \cdot A_S \cdot (C_{g,i,k} - C_{s,i,k}) \quad (1)$$

The mass transfer coefficient is calculated using bulk diffusion coefficients for NH_3 , NO , NO_2 , and N_2O from temperature dependent expressions readily available in the literature for studies of similar catalyst systems [21], and are summarized in Table 2.

$$k_{mt,i} = \frac{D_{bulk,i} \cdot Sh_i}{d_H} \quad (2)$$

The position dependent Sherwood number was calculated using the following correlation for square channels [9, 22]:

$$Sh_i = 2.98 + 8.827(1000 \cdot z_i)^{-0.545} \exp(-48.2 \cdot z_i) \quad (3)$$

$$z_i = \frac{x \cdot D_{bulk,i}}{u_x \cdot d_H^2} \quad (4)$$

For each tank considered, the intrapore diffusion and reaction of NH_3 , NO , NO_2 , and N_2O throughout the catalyst washcoat phase was modeled, assuming the AMOX/SCR contributions to the reaction rate are proportional to their volumetric fractions:

$$D_{eff,i} \frac{d^2 C_{wc,i}}{dr^2} + \sum_{cat}^{AMOX,SCR} (\phi_{cat} \cdot \rho_{cat} \cdot R'_{cat,i}) = 0 \quad (5)$$

To calculate the concentration profiles through the washcoat layer at a given location in the monolith, we introduce the following boundary conditions for the washcoat layer. At the surface of the top washcoat layer (tl), the steady-state assumption entails that the mass transfer across the gas film is equal to the flux of mass into the washcoat phase (eq. 6). At the interface between the bottom layer/washcoat (bl) and the monolith wall, no concentration gradient is present (eq. 7):

$$D_{eff,tl,i} \left. \frac{dC_{wc,i}}{dr} \right|_{g/tl} = k_{mt,i} \cdot A_s (C_{g,i,k} - C_{s,i,k}) \quad (6)$$

$$\left. \frac{dC_{wc,i}}{dr} \right|_{wc/wall} = 0 \quad (7)$$

For cases where there are two catalyst layers with different diffusivity, one needs to specify the boundary conditions at the interface between the layers as well. The first boundary condition given by equation 8 states that the flux of a species diffusing out of the top layer is equal to the flux of a species diffusing into the bottom layer.

$$D_{eff,tl,i} \left. \frac{dC_{wc,i}}{dr} \right|_{tl,interface} = D_{eff,bl,i} \left. \frac{dC_{wc,i}}{dr} \right|_{bl,interface} \quad (8)$$

The second boundary condition for the interface is an equation of continuity for the different species at the interface.

$$C_{wc,i} \Big|_{tl,interface} = C_{wc,i} \Big|_{bl,interface} \quad (9)$$

The effective diffusion coefficient in the catalyst washcoat phase, $D_{eff,i}$ is calculated using the mean transport pore model [23], which accounts for contributions from both bulk and Knudsen diffusion. The mean transport pore model was chosen over more complex models, such as the random pore model, to limit model complexity [14, 23–25].

$$D_{eff,i} = \frac{\epsilon}{\tau} \cdot \left(\frac{1}{D_{bulk,i}} + \frac{1}{D_{K,i}} \right)^{-1} \quad (10)$$

The values of the porosity, ϵ , and tortuosity, τ , are set to 0.4 and 3, respectively, which are common and realistic values [26]. As previously mentioned, the bulk diffusion coefficients, $D_{bulk,i}$, for NH_3 , NO , NO_2 , and N_2O were calculated using the expressions in Table 2 [21]. The Knudsen diffusion coefficient, $D_{K,i}$, was calculated using equation 11 [23]:

$$D_{K,i} = \frac{d_{pore}}{3} \sqrt{\frac{8 \cdot R \cdot T}{M_{w,i} \cdot \pi}} \quad (11)$$

The values for the average pore diameters, d_{pore} , were estimated by fitting the model against the experimental data for the monolithic ASC samples.

The monolith model was implemented in MATLAB and the *bvp4c* function was used to solve the boundary value problem of the monolith wall. For 10 tanks or more, the difference between solutions resulting from a change in the number of tanks was negligible, and therefore, we chose to use 10 tanks for our simulations. For the washcoat layer, a step size of 0.5 μm was used in the discretization.

3.2 Kinetic Models

In order to calculate the concentration profiles in the monolith reactor, the reaction rates in the washcoat layer must be known (see eq. 5). These reaction rates are derived from kinetic models for the 1 wt.% Pt/TiO₂ AMOX catalyst and the 3.5 wt.% Cu-Beta SCR catalyst. These models were developed based on activity measurements from fixed bed reactors and a reactor model for the fixed bed reactor. We used the *lsqcurvefit* function in MATLAB to fit the pre-exponential factor and the activation energy (A_j , $E_{A,j}$). The objective function was set to minimize the difference between simulated and experimental outlet concentrations of the reactants and products ($i = \text{NH}_3$, NO, NO₂, N₂O, and N₂), as given by equation 12:

$$\min_{A_j, E_{A,j}} = \sum_i \left(y(A_j, E_{A,j})_{sim,i} - y_{exp,i} \right)^2 \quad (12)$$

For the fixed bed reactor, we assumed ideal plug flow, steady-state, isothermal, and isobaric conditions. Equation 13 describes the fixed bed reactor material balance in terms of the gas phase concentration:

$$Q \cdot \frac{dC_{g,i}}{dW} = R'_{cat,i} \quad (13)$$

The material balance for the adsorbed phase is simplified by the steady-state conditions:

$$\Omega_i \frac{d\theta_i}{dt} = 0 \quad (14)$$

The catalytic mass based rate of reaction for each reactant i is expressed by equation 15 and the reaction rate coefficient from the Arrhenius expression (equation 16). During fitting of the kinetic

parameters, a reformulation of equation 16 was used to decouple A_j and $E_{A,j}$ [27]. For conversion from mass to volume based reaction rates, the following catalyst densities are used $\rho_{AMOX} = 1127 \text{ kg}_{cat}/\text{m}^3$ and $\rho_{SCR} = 954 \text{ kg}_{cat}/\text{m}^3$.

$$R'_{cat,i} = \sum_{j=1}^{N_r} \nu_{i,j} \cdot r'_j(p_i, \theta_i, k_j) \quad (15)$$

$$k_j = A_j \exp\left(-\frac{E_{A,j}}{R \cdot T}\right) \quad (16)$$

3.2.1 Kinetic Model for the Ammonia Oxidation Catalyst

In this paper we are interested in a simple kinetic models giving a good representation of the overall reactions, and not a full micro-kinetic model. First, we establish a simple kinetic model for NH_3 oxidation catalyzed by the 1 wt.% Pt/TiO₂ to describe the oxidation of NH_3 over the AMOX catalyst. The relevant reactions for this model are summarized in Table 3. These include the adsorption and desorption of NH_3 on the catalyst surface (AMOX.1), the oxidation of adsorbed NH_3 to N_2 (AMOX.2) and NO (AMOX.3), the oxidation of NH_3 and NO to N_2O (AMOX.4) [5, 8, 12, 28] and the oxidation of NO to NO_2 (AMOX.5f). The oxidation of NO is a reversible reaction and the reverse reaction is included as the decomposition of NO_2 (AMOX.5b) [11, 12, 21]. The equilibrium constant for this reaction was calculated from thermodynamic data [29] to ensure thermodynamic consistency.

Under typical reaction conditions, the amounts of H_2O and O_2 are much larger than those of the key reactants and products (NH_3 , NO , NO_2 , and N_2O). Therefore, the concentrations of H_2O (5 vol. %) and O_2 (10 vol. %) have been kept constant and do not appear explicitly in the rate equations. The only exception is the rate expression for NO oxidation and NO_2 decomposition (AMOX.5f), where the O_2 concentration is included.

3.2.2 Kinetic Model for the Selective Catalytic Reduction

To describe the SCR reaction over the 3.5 wt.% Cu-Beta catalyst, we adopted the kinetic model for Cu-CHA proposed by Metkar et al. [21]. The reactions and associated rate expressions are listed in Table 4. The reactions include NH_3 adsorption and desorption on the catalyst (SCR.1), NH_3 oxidation (SCR.2), NO oxidation (SCR.3f), and NO_2 decomposition (SCR.3b). In contrast to the Pt-based AMOX catalyst, the NH_3 oxidation reaction on Cu-Beta primarily leads to the formation of N_2 , with NO and N_2O being formed in rather insignificant quantities [10, 21, 30]. Therefore, we only consider N_2 as the product of NH_3 oxidation. The oxidation of NO and the decomposition of NO_2 was handled in the same manner as for the AMOX catalyst, using the thermodynamic equilibrium [29]. The SCR reactions included in the model are: standard (SCR.4), slow (SCR.6), and fast (SCR.8).

A difference between the Cu-Beta and Cu-CHA catalyst is that a Cu-Beta catalyst has a higher selectivity for the formation of N_2O . Formation of N_2O has been attributed to the decomposition of an NH_4NO_3 intermediate, which forms from reaction of NH_3 and NO_2 [21, 30]:

The reaction between adsorbed NH_3 and NO_2 (SCR.7), based on reaction (R.1), accounts for the formation of N_2O in the presence of NO_2 . However, N_2O is also formed only in the presence of NO . One possible explanation is found in the mechanism for the standard SCR reaction proposed by Janssens et al. [4], in which NO_2 is formed in the catalytic cycle. Therefore, we also include a reaction between NH_3 and NO (SCR.5), similar to reaction SCR.4, to account for N_2O formation from a feed gas without NO_2 . These two reactions (SCR.5 and SCR.7) account for the majority of N_2O formed during fast SCR conditions, but are not enough to account for all N_2O formed. As a result, it was necessary to include an extra N_2O contribution, due to an enhanced N_2O formation in the presence of both NO and NO_2 (SCR.9), similar to the improved rate of reaction during fast SCR conditions. By including the partial pressures of both NO and NO_2 in the rate expression, it is ensured that the reaction is only considered under fast SCR conditions, even though it only consumes NO_2 .

With regard to the standard SCR reaction, it has been reported in the literature [31–34] that the NO conversion versus temperature over Cu-zeolites is atypical. The NO conversion increases with temperature as expected until about 225–250°C, at which point the conversion decreases to a local minimum at about 350°C, before increasing again [34]. This behavior corresponds to a gradual transition between a low temperature reaction route which peaks at 250°C and a high temperature reaction route that dominates at temperatures above 350°C. At temperatures below 250°C, isolated Cu sites cannot activate O_2 independently, and two mobile $[\text{Cu}(\text{NH}_3)_2]^+$ ions are needed, forming an $[\text{Cu}(\text{NH}_3)_2]^+ - \text{O}_2 - [\text{Cu}(\text{NH}_3)_2]^+$ intermediate [34–36]. When the temperature increases, the Cu ions are immobilized by desorption of the NH_3 ligand, and the activation of O_2 now occurs on isolated Cu^I sites, with an increased reaction barrier [34–36].

To account for this transition in the kinetic model, two sets of kinetic parameters for the standard SCR and corresponding N_2O formation were included in the model; one set for each kinetic regime. To weigh the contribution of the low (mobile Cu sites) and high (immobilized Cu sites) temperature kinetics, a fractional weighting given by x_{LT} and $x_{HT} = 1 - x_{LT}$ with values between 0 and 1 was applied. The balance and transfer between the kinetic regimes was modeled similar to a Langmuir adsorption equilibrium reaction (SCR.10), with an equilibrium constant expressed using the following version of the Van't Hoff equation:

$$K_{eq,x} = \exp\left(\frac{-\Delta H + T \cdot \Delta S}{R \cdot T}\right) \quad (17)$$

The values for the change in reaction enthalpy, ΔH , and entropy, ΔS , were estimated by a parameter fitting. The fractions of x_{LT} and x_{HT} are determined from the equilibrium constant and the relationship between x_{LT} and x_{HT} :

$$x_{LT} = \frac{1}{1 + K_{eq,x}} \quad (18)$$

$$x_{HT} = 1 - x_{LT} \quad (19)$$

Table 4 summarizes the reactions and rate expressions in our kinetic model for the 3.5 wt.% Cu-Beta SCR catalyst.

3.3 Multi-Objective Optimization

The design of an ASC is a multi-objective optimization problem since the goal is to minimize emissions of NH_3 , NO_x , and N_2O , as well as the cost, size, and weight of the ASC. For simplicity, we here focus on minimizing emissions and disregard the other design objectives. Furthermore, we will consider an

equal N-based weighting for NH₃, NO_x, and N₂O slip. An optimal set of values for the design parameters therefore results in the lowest total emissions of NH₃, NO_x, and N₂O. Due to the trade-off that occurs between NH₃ conversion (equation 20) and the formation of either N₂ or emissions of NO_x and N₂O (equation 21-23) for the ASC, there exist many possible combinations of NH₃, NO_x, and N₂O outlet concentrations that provide the lowest total emissions, all with their respective set of parameter values.

$$\text{NH}_{3,\text{conv}} = \frac{C_{g,\text{NH}_3,\text{in}} - C_{g,\text{NH}_3,\text{out}}}{C_{g,\text{NH}_3,\text{in}}} \quad (20)$$

$$\text{N}_2\text{O}_{\text{selec}} = \frac{2 \cdot C_{g,\text{N}_2\text{O},\text{out}}}{C_{g,\text{NH}_3,\text{in}} - C_{g,\text{NH}_3,\text{out}}} \quad (21)$$

$$\text{NO}_{x,\text{selec}} = \frac{C_{g,\text{NO}_x,\text{out}}}{C_{g,\text{NH}_3,\text{in}} - C_{g,\text{NH}_3,\text{out}}} \quad (22)$$

$$\text{N}_{2,\text{selec}} = 1 - \text{N}_2\text{O}_{\text{selec}} - \text{NO}_{x,\text{selec}} \quad (23)$$

This is common for multi-objective problems and the set of optimal solutions forms a front reflecting the trade-off known as a Pareto front. This concept is illustrated for the ASC in Figure 3, where the sum of NO_x and N₂O slip is plotted against NH₃ slip. The ideal solution occurs for 0 ppm NH₃ slip and 0 ppm (NO_x + 2x N₂O slip), corresponding to 100% N₂ yield (origin in green region). The optimal solutions are those closest to the ideal solution and they form the Pareto front (solid green circles connected by solid black lines). The remaining solutions are non-optimal (red crosses). The multi-objective optimization was performed for each of the ten different ASC configurations presented in Figure 2 by optimizing a bound set of parameters: Pt loading (intrinsic activity) of AMOX catalyst (Pt = 0.01–6.11 wt.% Pt on TiO₂ and maximum of 61.1 mg Pt/L_{monolith}), AMOX catalyst loading (AMOX = 1–60 g/L_{monolith}), SCR catalyst loading (SCR = 1–200 g/L_{monolith}), and average pore diameter (effective diffusivity) of catalyst layers (d_{pore} = 40–200 nm). These ranges and constraints were chosen to limit the system to reasonable design parameters.

The overall objective of the ASC optimization was the minimization of NH₃, NO_x, and N₂O emissions. It should be noted that the optimization result is affected by the weighting, and as mentioned, an equal weighting based on the N atoms was applied to each emission. The resulting objective function for the multi-objective optimization problem was:

$$\min_{w_{\text{AMOX}}, w_{\text{SCR}}, d_{\text{pore}}, \chi_{\text{Pt}}} f = [\text{NH}_3]_{\text{out}} + [\text{NO}_x]_{\text{out}} + 2 \times [\text{N}_2\text{O}]_{\text{out}} \quad (24)$$

The optimization was completed using MATLAB's *gamultiobj* function, which employs the genetic algorithm for multi-objective optimization [37–39]. The genetic algorithm applies concepts of natural selection in biological evolution, to iteratively optimize a set of parameters for a given optimization problem [37]. In short, the optimization starts with a number of initial guesses, and for each guess, a score is determined according to the objective function (eq. 24). The next generation of guesses is generated, by changing and combining the initial guesses, where the score guides the probability that a given parameter set is included or not. By repeating this process, the parameter sets eventually evolve to the Pareto set. In this study, we have used a set of 50 initial guesses, multiplied by the number of parameters to vary, to account for the increase in possible solutions with the increase in parameters for the more complex configurations. The optimization was stopped after 10 iterations. The Pareto fronts resulting from the final set of optimal solutions were used to evaluate the sensitivity

of the ASC performance to the possible ASC configurations. Further details can be found in supporting information.

4. Results

4.1 Validation of the Kinetic Models

Before we evaluate the performance of the different ASC configurations, we validate the kinetic models for ASC and SCR components separately. To validate the kinetic model for the ammonia oxidation catalyst, we have fitted the experimentally determined conversions of NH_3 and the corresponding product distributions for the 1 wt.% Pt/TiO₂ AMOX catalyst in the temperature range 200–550°C, as measured in a powder reactor, using the reaction scheme in Table 3. The experimental and calculated data are compared in Figure 4; the corresponding kinetic parameters of the model fit are presented in Table 3. The good agreement between the measured and calculated values indicates that our model provides a satisfactory description of the behavior of the 1 wt.% Pt/TiO₂ AMOX catalyst.

The experimental data for NH_3 oxidation show a steep decrease of the NH_3 concentration as the temperature is increased from 200°C to 250°C, reaching 50% conversion at 229°C and 100% at 250°C. The N_2 selectivity is high between 200–250°C, with a maximum of 75% N_2 selectivity at 230°C. The N_2O formation steeply increases at temperatures above 220°C as the N_2 selectivity decreases, and a maximum of 49% N_2O selectivity at 270°C is observed. Above 250°C, the formation of NO becomes increasingly significant, while the product selectivity towards N_2 and N_2O decreases simultaneously. Furthermore, the formation of NO_2 is seen to increase from 275°C to a maximum of 100 ppm NO_2 at 450°C (20% NO_2 selectivity). The maximum in NO_2 is a result of the thermodynamic equilibrium for the $\text{NO} + \frac{1}{2} \text{O}_2 \leftrightarrow \text{NO}_2$ reaction, which shifts towards NO above 450°C [40]. The model contains some rate coefficients with activation energies between 187–303 kJ/mol, which are necessary to describe the steep increase in NH_3 conversion between 200 and 250°C. We note that these are very high values for the activation energy. This indicates that the description of the NH_3 ammonia oxidation reaction used here is probably too simple. Nevertheless, it describes the observed behavior of the Pt catalysts well, which is sufficient for modeling the catalytic performance.

Figure 5 shows a comparison of the measured and calculated conversions and product distributions for the performance of the 3.5 wt.% Cu-Beta catalyst, the SCR component, using the reaction scheme in Table 4. For this SCR catalyst, we have considered (A) the oxidation of NH_3 , (B) NO oxidation, (C) NO_2 decomposition, (D) standard SCR ($\text{NO}_2/\text{NO}_x=0$), (E) slow SCR ($\text{NO}_2/\text{NO}_x=1$), and (F) fast SCR ($\text{NO}_2/\text{NO}_x=0.5$). The conditions for these reactions have been obtained by adjusting the concentrations of NH_3 , NO, and NO_2 in the reaction feed gas. For Figure 5 D, E, and F, the two points at 225°C are the result of overlap in measurements done with respectively 40 and 20 mg catalyst. The kinetic parameters determined from parameter fitting, of the kinetic model for the SCR catalyst are presented in Table 4. For all reactions, the measured and calculated data show good agreement, indicating that the reaction scheme describes the behavior of the Cu-Beta SCR catalyst well.

From Figure 5 A, the 3.5 wt.% Cu-Beta catalyst becomes active for the oxidation of NH_3 by O_2 at about 300°C, and reaches 80% conversion at 500°C. This oxidation is very selective towards N_2 with only 5 ppm N_2O and 22 ppm NO_x , which supports the decision not to include NH_3 oxidation to NO_x or N_2O in the SCR kinetic model. Furthermore, the oxidation of NO to NO_2 , and the NO_2 decomposition (Figure 5 B and C) are quite slow compared to the Pt/TiO₂ catalyst applied in this study.

The catalytic activity of the Cu-Beta catalyst for the standard SCR reaction is shown in Figure 5 D. Between 250 and 350°C, the conversion of NO and NH_3 changes less than one would expect from an

Arrhenius-like behavior. Such behavior is known for NH_3 -SCR over Cu-zeolite based catalysts, in particular Cu-CHA, and is sometimes also observed as a decrease in NO_x conversion [31, 32, 34, 35]. This behavior is an indication that the NH_3 -SCR reaction follows different mechanisms at low and high temperatures [34]. As discussed above, the kinetic model developed here for the Cu-Beta SCR catalyst includes a temperature dependent transition between two kinetic regimes of the standard SCR reactions (SCR.4 and SCR.5). The simulated NO_x conversion for the standard SCR operating conditions between 150–550°C is illustrated in Figure 6. The contribution from each of the respective rate expressions is controlled by the fractions x_{LT} and x_{HT} as noted in Table 4. At temperatures below 220°C, the standard SCR kinetics are 90% controlled by the low temperature kinetics. Above 220°C, the contribution from the low temperature kinetics becomes smaller, reaching 50% at 260°C and 10% at 310°C. By including this transition between the kinetic regimes of the standard SCR reactions (SCR.4 and SCR.5) in the kinetic model, it is able to accurately describe the non-Arrhenius behavior of the Cu-Beta catalyst for standard SCR.

4.2 Validation of the Monolith Model

In this section, the monolith ASC model is described and validated. To validate the ASC model, we compared measured outlet concentrations of NH_3 , N_2 , NO_x , and N_2O for NH_3 oxidation with calculated values according to the kinetics derived in Sections 3.2.1 and 3.2.2, as shown in Figure 7. The effective diffusivities of the gases in the catalyst layers are not known a priori, and therefore, the values for the diffusion coefficients are adjusted to fit the experimental data. To obtain a consistent set of diffusion coefficients for the different gases, the average pore diameter in each catalyst layer is varied manually to calculate the effective diffusion coefficients according to eqs. 10 and 11. With a pore diameter 50 nm, corresponding to $D_{\text{eff}} = 1.38 \times 10^{-6} \text{ m}^2/\text{s}$ at 200°C for NH_3 , we find a good agreement between measured and calculated values for each catalyst layer in the single layer AMOX, single layer SCR, and dual layer configurations. For the single mixed layer catalyst, good agreement is obtained for a pore diameter of 15 nm, corresponding to $D_{\text{eff}} = 0.48 \times 10^{-6} \text{ m}^2/\text{s}$ at 200°C for NH_3 . This lower diffusion coefficient result from the intermixing and void filling of two powders with different particle sizes.

Figure 7 shows that the model describes the conversion of NH_3 and the main trends in the product distributions well. The model follows the trend that a single layer AMOX catalyst has a high selectivity for NO_x , which is significantly reduced by adding an SCR component. The formation of N_2O over the AMOX catalyst is underestimated by the model in the temperature range 200–300°C, due to a too high selectivity for N_2 , but the trend that the presence of an SCR component reduces the formation of N_2O is reproduced. The differences between experimental and calculated data are similar to those observed in other studies [6, 10–12]. Therefore, we conclude that the monolithic model, using the kinetic models based on fixed bed reactor data, reflects the behavior of the different catalyst systems quite well, which validates ASC model for our purpose.

4.3 Optimization of ASC Configurations

To further improve the understanding of the interplay between SCR and AMOX components in an ASC system, the expected performance of the ten possible ASC configurations shown in Figure 2 is calculated using the monolith model. In this study we focus on the effects of the loadings of SCR and AMOX catalyst, Pt loading (intrinsic activity) of the AMOX catalyst, and the average pore diameter (effective diffusivity) in the catalyst layers, for the ten configurations of the ASC monolith. By varying these parameters, we construct Pareto fronts for NO_x slip, N_2O slip, combined NO_x and N_2O slip, and N_2 formed, all as a function of the NH_3 slip, because the NH_3 slip is the main performance parameter for an ASC. Table 5 summarizes the optimized data set, and the corresponding Pareto fronts are given

in Figure 8. For the optimization, we have fixed the temperature to 300°C, and otherwise used the same conditions as mentioned in the previous sections.

The Pareto fronts for the NO_x slip (Figure 8 A) reflect the ability of the different ASC configurations to oxidize NH₃ without forming NO_x. For the majority of catalysts, the Pareto fronts overlap at a low NO_x slip; these catalysts all effectively have a mixed top layer. Two catalysts stand out in the graph, namely that for the single layer AMOX catalyst and the inverse dual layer configuration. In both configurations, the Pt/TiO₂ catalyst is exposed directly to the gas phase. The single layer AMOX catalyst produces the most NO_x, and this is the known issue with this catalyst design [3, 5–13, 15, 17, 19, 20], and the reason why an SCR component is usually added to the ASC. The inverse dual layer consists of a top layer of AMOX catalyst, on a bottom layer of the SCR catalyst. Therefore, it is also quite active in NO_x formation, although the presence of the SCR bottom layer greatly improves its N₂ selectivity, compared to the single layer AMOX catalyst. The hybrid dual layer with an AMOX top layer, also leads to a significant NO_x slip. However, since this configuration has the option of mixing a significant part of the AMOX catalyst together with the SCR catalyst in the bottom layer, the selectivity for NO_x becomes lower than for the inverse dual layer configuration. Finally, the dual layer and the hybrid dual layer with an SCR top layer have a significant NO_x slip at high NH₃ conversion, because high ammonia conversion comes with an increased accessibility to the AMOX catalyst, leading to an increase in NO_x formation. This means that in these configurations, the NO_x slip is always lowered at the cost of NH₃ conversion.

In the trade-off for NH₃ conversion and N₂O formation (Figure 8 B), the optimized single layer AMOX, dual layer, and inverse dual layer catalysts show the highest N₂O selectivity. The largest contribution for N₂O formation comes from the reaction of NO and NH₃ over Pt (Table 3, AMOX.4). These catalyst configurations contain a single pure layer of AMOX catalyst, which thus leads to a high N₂O formation. Unexpectedly, the N₂O slip from the hybrid dual layer with an AMOX top layer configuration is one of the lowest even though the catalyst includes a pure top layer of AMOX catalyst. This is due to a combination of a moderate intrinsic activity of the AMOX catalyst and a high effective diffusivity, which limits the reaction between NH₃ and NO to N₂O over the AMOX catalyst. All catalysts with mixed layers of AMOX and SCR catalyst show a low N₂O slip, since the SCR catalyst ensures a fast reaction between NO_x and NH₃ leaving little chance for these species to react to N₂O over the AMOX catalyst.

Figure 8 C shows the Pareto fronts for the combination of the NO_x slip and N₂O slip, which is the objective function that has been used in the optimization (eq. 12). In general, the observations are similar to those from Figure 8 A and B: The catalysts that are most selective in oxidizing NH₃ to NO_x and N₂O are the single layer AMOX, inverse dual layer, and dual layer, while the mixed layer catalysts are overlaying, and the least selective towards NO_x and N₂O (most selective to N₂).

The Pareto fronts for the N₂ formation (Figure 8 D) represent the optimized yields of N₂ that can be obtained for the different ASC configurations. The dashed gray line represents the N₂ selectivity of an ideal ASC, for which NH₃ is only oxidized to N₂. For most curves, a maximum in these curves indicates an optimal solution for the given configuration. From Figure 8 D, we see that the most effective catalysts for oxidizing NH₃ to N₂ are those that contain mixed layers in the top. By combining the AMOX and SCR components, the NH₃ oxidation activity is balanced with the NO_x reduction leading to a significant improvement in the selective oxidation of NH₃ to N₂.

A comparison of the composition of the ten ASC configurations at their peak performance (minimum in the objective function, Table 5), shows that the configurations generally favor a high effective diffusivity (max d_{pore} of 200 nm) and use almost all the available SCR and Pt (maximum allowable

levels of 200 g/L_{monolith} and 61.1 mg_{Pt}/L_{monolith}). The most efficient utilization of the raw materials is obtained for configurations with mixed layers, in particular the dual mixed layer, hybrid dual layer with an AMOX top layer, and inverse hybrid dual layer with SCR bottom layer configurations.

5. Discussion

The results from multi-objective optimization of the ten different ASC configurations presented contribute to the understanding of the ASC. In general, the performance of the ASC is highly dependent on the Pt loading (mg_{Pt}/L_{monolith}), since an absence of Pt results in a lack of NH₃ oxidation activity. This is most clearly observed at temperatures below 300°C where the rate of NH₃ oxidation is limited by the reaction kinetics. However, if the oxidation activity is sufficiently high, the rate of NH₃ oxidation becomes controlled by internal or external mass transfer limitations. At this point, the catalyst loading (layer thickness) and effective diffusivity of the catalyst layers become increasingly significant.

The thickness of the catalyst layer is affected by variations in catalyst loading, and this also affects the rate of the diffusion through catalyst layers. As a consequence, it is more beneficial to apply a low loading of an AMOX catalyst with a higher Pt loading (catalyst with high intrinsic activity), thereby keeping diffusion limitations to a minimum. Especially for the dual layer catalyst, diffusion properties are an important design parameter, since the SCR top layer is acting as a diffusion barrier for NH₃ to the AMOX catalyst, while also providing the necessary SCR activity. This has also been shown by recent investigations where macro-porosity was introduced into the SCR layer of a dual layer ASC using yeast or polymers, to enhance mass transport to the AMOX layer [16]. For the single mixed layer catalyst, the key design parameter is the SCR catalyst loading since it is used to balance the NH₃ oxidation activity with the SCR activity, in effect determining product selectivity of the ASC. The effective diffusivity is still significant in ensuring a high effectiveness factor, but is less critical than the SCR loading for the dual layer catalysts.

In our simulations, the mass transfer resistance in the catalyst layers is described by the diffusion coefficients in these layers. We have estimated the diffusion coefficients by including the contribution of Knudsen diffusion (eqs. 10 and 11) and have adjusted the pore diameters in the catalyst layers, using constant values of the porosity ($\epsilon = 0.4$) and tortuosity ($\tau = 3$); these are typical values for randomly packed beds. Using pore diameters of 15 and 50 nm, which is in the correct order of magnitude for a washcoat layer [24], we obtain values of the diffusion coefficients that result in the experimentally observed conversion levels. Neglecting Knudsen diffusion for pore sizes in this range may lead to using unrealistic values of the tortuosity to fit the data from washcoated monoliths [12].

The multi-objective optimization of the ten ASC configurations points to the combinations of intrinsic activity, catalyst loading, and effective diffusivity, that lead to minimal emissions for a given catalyst configuration. Based on the solutions we have found, it becomes clear that ASC configurations with mixed layers perform best and utilize the catalyst material most efficiently, as seen in the following ranking:

$$\left(\frac{\text{AMOX+SCR}}{\text{AMOX+SCR}}\right) \approx \left(\frac{\text{AMOX}}{\text{AMOX+SCR}}\right) \approx \left(\frac{\text{AMOX+SCR}}{\text{SCR}}\right) > \left(\frac{\text{SCR}}{\text{AMOX+SCR}}\right) \approx \left(\frac{\text{AMOX+SCR}}{\text{AMOX+SCR}}\right) > \left(\frac{\text{AMOX+SCR}}{\text{AMOX}}\right) > \left(\frac{\text{AMOX}}{\text{SCR}}\right) > \left(\frac{\text{SCR}}{\text{AMOX}}\right) >> \left(\frac{\text{AMOX}}{\text{AMOX}}\right) > \left(\frac{\text{SCR}}{\text{SCR}}\right)$$

According to our current understanding, there are two factors that determine this behavior. First, the good accessibility of the AMOX component ensures a high conversion of NH₃. Second, the immediate vicinity of the SCR catalyst reduces the concentrations of NO and NH₃ at the Pt-based AMOX catalyst, thus avoiding formation of unwanted N₂O and improving the selectivity to N₂.

It should be emphasized that the validity of the optimization presented can be further expanded. First, we have used a single temperature of 300°C and fixed other conditions, such as flow and feed gas composition (i.e. no NO_x in the feed). Furthermore, a transient model allowing for variable inlet gas composition, flow rate and temperature would enable a more direct comparison with real world applications. The second limitation is that the result depends on the relative weighting of the emissions in the objective functions. These limitations will influence the outcome of the optimization. For example, an SCR top layer could be more advantageous if NO_x is present in the feed along with NH₃ or at higher temperatures where the SCR catalyst is active for selective oxidation of NH₃. Furthermore, in our optimization, the NH₃ conversion was weighted equally with NO_x and N₂O selectivity, but this is an arbitrary choice, and a different weighting of these factors will result in different optimized formulations. Our approach of combining reactor models and relevant design parameters to determine Pareto fronts, offers a useful tool to evaluate the effect of the design parameters simultaneously, and decide how to balance the different properties, such as activity, diffusivity, and amounts of catalyst, in order to reach the optimal performance.

6. Conclusion

An ammonia slip catalyst (ASC) combines the high activity of the ammonia oxidation (AMOX) catalyst with the efficiency of selective catalytic reduction of NO_x with NH₃ over an SCR catalyst (NH₃-SCR), to ensure minimal NH₃ slip and limited formation of NO_x and N₂O.

In order to investigate and compare optimal solutions of different ASC configurations, an extensive flow reactor study using powder catalysts was carried out to determine the intrinsic kinetics of the relevant reactions over 1 wt.% Pt/TiO₂ (AMOX) and 3.5 wt.% Cu-Beta (SCR). The Cu-Beta SCR kinetic model accounts for the non-Arrhenius behavior, by a transition between low temperature and high temperature kinetics. A 1D-1D (pseudo 2D) mathematical model of a monolithic ASC, implementing the derived intrinsic kinetics of the catalysts, was developed and fitted to experimental data using four different small scale monoliths, using the pore size of the ASC layers as fitting parameter. The model describes well the NH₃ conversion and NO_x yields, and to a reasonable extent the yields of N₂O and N₂ over the four small scale monoliths.

The performance of ten different ASC configurations was investigated by using the model to perform a multi-objective optimization of NH₃ oxidation at 300°C, by varying the intrinsic activity of the AMOX catalyst (Pt content), the loadings of the AMOX and SCR catalysts, and the effective diffusivity of the catalyst layers. The resulting Pareto fronts indicate that the most effective catalyst designs are those that contain a thin top layer, has high effective diffusivity in the layers, and use a high mixed layer load.

Catalyst configurations with pure layers of AMOX catalyst generally produce the most N₂O, identifying the Pt-based AMOX catalyst as the main source of N₂O. In configurations with only an SCR catalyst in the top layer, the NH₃ conversion can be increased using either a thinner or a more open layer of the SCR catalyst, since the top layer acts as a diffusion barrier for NH₃ to reach the AMOX catalyst. This, however, leads to a high NO_x selectivity at high NH₃ conversion. Overall, ASC's with mixed layers provide the highest NH₃ conversion, due to the accessibility to the AMOX catalyst for NH₃, while SCR catalyst in the immediate vicinity keeps the concentrations of NO_x and NH₃ at a low level, which suppresses the formation of N₂O over the AMOX catalyst.

Declarations

Conflict of Interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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Nomenclature

Abbreviations:

AMOX	Ammonia oxidation
ASC	Ammonia slip catalyst
cpsi	Cells per square inch
FTIR	Fourier-transform infrared spectroscopy
GHSV	Gas hourly space velocity (hr^{-1})
NO_x	Nitrogen oxides (NO and NO_2)
SCR	Selective catalytic reduction

Arabic Letters:

A	Pre-exponential factor $\left(\frac{\text{mol}}{\text{s} \cdot \text{kg}_{\text{cat}}}, \frac{\text{mol}}{\text{s} \cdot \text{kg}_{\text{cat}} \cdot \text{bar}}, \frac{\text{mol}}{\text{s} \cdot \text{kg}_{\text{cat}} \cdot \text{bar}^2}, \frac{\text{mol}}{\text{s} \cdot \text{kg}_{\text{cat}} \cdot \text{bar}^2} \right)$
A_s	External surface area of catalyst washcoat per tank (m^2)
C_g	Gas phase concentration (mol/m^3)
C_s	Concentration at the surface of the catalyst washcoat (mol/m^3)
C_{wc}	Concentration in the washcoat phase (mol/m^3)
D_{bulk}	Bulk diffusion coefficient (m^2/s)
D_{eff}	Effective diffusion coefficient (m^2/s)
D_K	Knudsen diffusion coefficient (m^2/s)
d	Diameter of monolith sample (m)
d_H	Hydraulic diameter of the coated channel (m)
d_{pore}	Average pore diameter (m)
E_A	Activation energy (J/mol)
f	Fitness function (ppm)
K_{eq}	Equilibrium constant for thermodynamic equilibrium of NO and NO_2 ()
$K_{eq,x}$	Equilibrium constant for describing transfer between kinetic regimes of SCR catalyst ()
k	Reaction rate coefficient $\left(\frac{\text{mol}}{\text{s} \cdot \text{kg}_{\text{cat}}}, \frac{\text{mol}}{\text{s} \cdot \text{kg}_{\text{cat}} \cdot \text{bar}}, \frac{\text{mol}}{\text{s} \cdot \text{kg}_{\text{cat}} \cdot \text{bar}^2}, \frac{\text{mol}}{\text{s} \cdot \text{kg}_{\text{cat}} \cdot \text{bar}^2} \right)$
k_{mt}	Mass transfer coefficient (m/s)
L	Length of monolith sample (m)

N_r	Total number of reactions
n_{param}	Number of parameters being varied in the multi-objective optimization ()
n_{gen}	Number of generations being evaluated in the multi-objective optimization ()
M_w	Molar mass (kg/m ³)
$N_{2,selec}$	Product selectivity towards N ₂ ()
N_2O_{selec}	Product selectivity towards N ₂ O ()
$NH_{3,conv}$	Ammonia conversion ()
$NO_{x,selec}$	Product selectivity towards NO _x ()
p	Partial pressure (bar)
Q	Volumetric flow (m ³ /s)
R	Gas constant (J/(K mol))
R'	Total rate of reaction (mol/(kg s))
r	Radial position (m)
r'	Rate of reaction (mol/(kg s))
Sh	Sherwood number ()
T	Temperature (K)
t	Time (s)
u_x	Linear gas velocity (m/s)
W	Catalyst mass (kg)
w_{AMOX}	Load of AMOX catalyst (g/L)
w_{SCR}	Load of SCR catalyst (g/L)
x	Axial position in the monolith channel (m)
x_{LT}	Contribution from low temperature Cu sites to SCR kinetics ()
x_{HT}	Contribution from high temperature Cu sites to SCR kinetics ()
y	Value for outlet concentrations used in parameter fitting (ppm)
z	Dimensionless position ()

Greek symbols:

Ω	Adsorption capacity of the catalyst (mol/kg _{cat})
θ	Surface coverage of the catalyst with adsorbed reactant ()
ΔH	Reaction enthalpy (J/mol)
ΔS	Entropy (J/(mol K))
ρ	Catalyst density (kg _{cat} /m ³)
ϕ	Volume fraction of catalyst in layer ()
ν	Stoichiometric reaction coefficient ()
ϵ	Porosity ()
τ	Tortuosity ()
χ_{Pt}	Pt content of AMOX catalyst (wt.%)

Subscript and superscript

<i>bl</i>	Bottom layer of ammonia slip catalyst
<i>cat</i>	Catalyst (AMOX or SCR)
<i>exp</i>	Experimental value
<i>g</i>	Gas phase
<i>g/tl</i>	Interface of between gas phase and top layer
<i>i</i>	Species <i>i</i>
<i>in</i>	Inlet
<i>interface</i>	Interface between bottom layer and top layer
<i>j</i>	Reaction <i>j</i>
<i>out</i>	Outlet
<i>sim</i>	Simulated
<i>tl</i>	Top layer of ammonia slip catalyst
<i>wall</i>	Monolith wall
<i>wc</i>	Catalyst washcoat phase
<i>wc/wall</i>	Interface between washcoat and monolith wall

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Tables and Figures:

Table 1: Overview of the monolithic ammonia slip catalysts prepared by dip coating with slurries of 1 wt.% Pt/TiO₂ (AMOX) and/or 3.5 wt.% Cu-Beta zeolite (SCR).

Sample	AMOX Loading (g _{wc} /L _{monolith})	Pt Loading (mg _{Pt} /L _{monolith})	SCR Loading (g _{wc} /L _{monolith})
Single layer AMOX	26	61.1	0
Single layer SCR	0	0	61
Single mixed layer	12	120	110
Dual layer	26	61.1	54

Figure 1: Illustration of the dual mixed layer (DML) ammonia slip catalyst configuration, which the ASC monolith model was based on.

Figure 2: The ten possible ammonia slip catalyst configurations that can be simulated using the dual mixed layer model. 1) single layer AMOX (SL-AMOX), 2) single layer SCR (SL-SCR), 3) dual layer (DL), 4) inverse dual layer (IDL), 5) hybrid dual layer with top layer of SCR (HDL-S), 6) inverse hybrid dual layer with bottom layer of SCR (IHDL-S), 7) hybrid dual layer with top layer of AMOX (HDL-A), 8) inverse hybrid dual layer with bottom layer of AMOX (IHDL-A), 9) single mixed layer (SML), and 10) dual mixed layer (DML).

Table 2: Expressions for the bulk diffusion coefficients as a function of temperature at atmospheric conditions [21].

Species	Diffusion Coefficient (m ² /s)
NH ₃	$1.215 \times 10^{-9} \cdot T^{1.7389}$
NO	$1.2365 \times 10^{-9} \cdot T^{1.7006}$
NO ₂	$7.9236 \times 10^{-10} \cdot T^{1.7297}$
N ₂ O	$8.1452 \times 10^{-10} \cdot T^{1.7314}$

Table 3: Kinetic model for the 1 wt.% Pt/TiO₂ AMOX catalyst at 5 vol.% H₂O and 10 vol.% O₂.

Reaction #	Reaction	Rate Expression ($\frac{\text{mol}}{\text{s} \cdot \text{kg}_{\text{cat}}}$)	A _j	E _{Aj} (kJ/mol)
AMOX.1f	NH ₃ + * → NH ₃ *	$k_{\text{AMOX.1f}} \cdot p_{\text{NH}_3} \cdot (1 - \theta_{\text{NH}_3})$	1.2×10^3	0
AMOX.1b	NH ₃ * → NH ₃ + *	$k_{\text{AMOX.1b}} \cdot \theta_{\text{NH}_3}$	1.3×10^9	91.0
AMOX.2	4 NH ₃ * + 3 O ₂ → 2 N ₂ + 6 H ₂ O + 4 *	$k_{\text{AMOX.2f}} \cdot \theta_{\text{NH}_3}$	2.0×10^{25}	258.8
AMOX.3	4 NH ₃ * + 5 O ₂ → 4 NO + 6 H ₂ O + 4 *	$k_{\text{AMOX.3f}} \cdot \theta_{\text{NH}_3}$	1.8×10^{29}	302.4
AMOX.4	4 NH ₃ * + 4 NO + 3 O ₂ → 4 N ₂ O + 6 H ₂ O + 4 *	$k_{\text{AMOX.4f}} \cdot \theta_{\text{NH}_3} \cdot p_{\text{NO}}$	4.5×10^{22}	187.8
AMOX.5f	NO + ½ O ₂ → NO ₂	$k_{\text{AMOX.5f}} \cdot p_{\text{NO}} \cdot p_{\text{O}_2}^{1/2}$	1.2×10^4	28.7
AMOX.5b*	NO ₂ → NO + ½ O ₂	$k_{\text{AMOX.5b}} \cdot p_{\text{NO}_2}$	—	—

* $k_{\text{AMOX.5b}} = \frac{k_{\text{AMOX.5f}}}{K_{\text{eq}}}$, equilibrium constant, K_{eq} , calculated from thermodynamic data [29].

Units for $A_{\text{AMOX.1b}}$, $A_{\text{AMOX.2}}$, and $A_{\text{AMOX.3}}$ are mol/(s · kg_{cat}).

Units for $A_{\text{AMOX.1f}}$, $A_{\text{AMOX.4}}$, and $A_{\text{AMOX.5b}}$ are mol/(s · kg_{cat} · bar).

Units for $A_{\text{AMOX.5f}}$ are mol/(s · kg_{cat} · bar^{3/2}).

Table 4: Kinetic model for the 3.5 wt.% Cu-Beta SCR catalyst at 5 vol.% H₂O and 10 vol.% O₂.

Reaction #	Reaction	Rate Expression ($\frac{\text{mol}}{\text{s} \cdot \text{kg}_{\text{cat}}}$)	A _j ^d	E _{Aj} (kJ/mol)
SCR.1f ^a	NH ₃ + * → NH ₃ *	$k_{\text{SCR.1f}} \cdot \frac{p_{\text{NH}_3}}{p_T} \cdot (1 - \theta_{\text{NH}_3})$	$6.68 \times 10^7 \cdot \rho_{\text{SCR}}^{-1}$	0
SCR.1b ^a	NH ₃ * → NH ₃ + *	$k_{\text{SCR.1b}} \cdot \theta_{\text{NH}_3}$	$4.00 \times 10^{15} \cdot \rho_{\text{SCR}}^{-1}$	$145.9 \cdot (1 - 0.97 \cdot \theta_{\text{NH}_3})$
SCR.2	4 NH ₃ * + 3 O ₂ → 2 N ₂ + 6 H ₂ O + 4 *	$k_{\text{SCR.2}} \cdot \theta_{\text{NH}_3}$	9.94×10^{10}	162.87
SCR.3f ^b	NO + ½ O ₂ → NO ₂	$k_{\text{SCR.3f}} \cdot p_{\text{NO}} \cdot p_{\text{O}_2}^{1/2}$	1.28×10^3	31.06
SCR.3b ^b	NO ₂ → NO + ½ O ₂	$k_{\text{SCR.3b}} \cdot p_{\text{NO}_2}$	—	—
SCR.4	4 NH ₃ * + 4 NO + O ₂ → 4 N ₂ + 6 H ₂ O + 4 *	$k_{\text{SCR.4LT}} \cdot \theta_{\text{NH}_3} \cdot p_{\text{NO}} \cdot x_{\text{LT}} + k_{\text{SCR.4HT}} \cdot \theta_{\text{NH}_3} \cdot p_{\text{NO}} \cdot x_{\text{HT}}$	LT: 1.56×10^{10} HT: 2.21×10^8	LT: 79.67 HT: 69.38
SCR.5	4 NH ₃ * + 4 NO + 3 O ₂ → 4 N ₂ O + 6 H ₂ O + 4 *	$k_{\text{SCR.5LT}} \cdot \theta_{\text{NH}_3} \cdot p_{\text{NO}} \cdot x_{\text{LT}} + k_{\text{SCR.5HT}} \cdot \theta_{\text{NH}_3} \cdot p_{\text{NO}} \cdot x_{\text{HT}}$	LT: 6.14×10^6 HT: 1.70×10^4	LT: 56.22 HT: 39.88
SCR.6	4 NH ₃ * + 3 NO ₂ → 7/2 N ₂ + 6 H ₂ O + 4 *	$k_{\text{SCR.6}} \cdot \theta_{\text{NH}_3} \cdot p_{\text{NO}_2}$	1.83×10^{18}	157.17
SCR.7	4 NH ₃ * + 4 NO ₂ → 2 N ₂ + 2 N ₂ O + 6 H ₂ O + 4 *	$k_{\text{SCR.7}} \cdot \theta_{\text{NH}_3} \cdot p_{\text{NO}_2}$	6.08×10^{16}	140.74
SCR.8	4 NH ₃ * + 2 NO + 2 NO ₂ → 4 N ₂ + 6 H ₂ O + 4 *	$k_{\text{SCR.8}} \cdot \theta_{\text{NH}_3} \cdot p_{\text{NO}} \cdot p_{\text{NO}_2}$	8.17×10^{23}	162.21
SCR.9	4 NH ₃ * + 4 NO ₂ $\xrightarrow{\text{NO}}$ 2 N ₂ + 2 N ₂ O + 6 H ₂ O + 4 *	$k_{\text{SCR.9}} \cdot \theta_{\text{NH}_3} \cdot p_{\text{NO}} \cdot p_{\text{NO}_2}$	2.65×10^{22}	149.25
SCR.10 ^c	$x_{\text{LT}} \rightleftharpoons x_{\text{HT}}$	$k_{\text{SCR.10f}} \cdot x_{\text{LT}} - k_{\text{SCR.10b}} \cdot x_{\text{HT}}$	—	—

^a Kinetic parameters from [21]. Units of mol/(s · m_{cat}³), divided by ρ_{SCR} to convert to mass based value with units of mol/(s · kg_{cat}).

^b $k_{\text{SCR.3b}} = k_{\text{SCR.3f}}/K_{\text{eq}}$, equilibrium constant, K_{eq} , calculated from thermodynamic data [29]

^c $k_{\text{SCR.10b}}/k_{\text{SCR.10f}} = K_{\text{eq},x} = \exp\left(\frac{-\Delta H - T\Delta S}{RT}\right)$, $\Delta H = 1.04 \times 10^5 \frac{\text{J}}{\text{mol}}$ and $\Delta S = 194.3 \frac{\text{J}}{\text{mol} \cdot \text{K}}$.

^d Units for $A_{\text{SCR.1b}}$ and $A_{\text{SCR.2}}$ are mol/(s · kg_{cat}).

^d Units for $A_{\text{SCR.1f}}$, $A_{\text{SCR.3b}}$, $A_{\text{SCR.4}}$, $A_{\text{SCR.5}}$, $A_{\text{SCR.6}}$, and $A_{\text{SCR.7}}$, are mol/(s · kg_{cat} · bar).

^d Units for $A_{\text{SCR.3f}}$ are mol/(s · kg_{cat} · bar^{3/2}).

^d Units for $A_{\text{SCR.8}}$ and $A_{\text{SCR.9}}$ are mol/(s · kg_{cat} · bar²).

Figure 3: Example of the Pareto front obtained through multi-objective optimization for the ASC system. Ideal solution: origin in green region of graph. Optimal solutions: solid green circles. Non-optimal solutions: red crosses.

Figure 4: Comparison of the NH_3 , NO , NO_2 , N_2O , and N_2 outlet concentrations for the oxidation of NH_3 over the 1 wt.% Pt/TiO_2 catalyst, based on the experimental data (symbols) and the model (solid lines) with the fitted kinetic parameters. Values for N_2 were calculated from the N-balance. Operating conditions: 5 mg 1 wt.% Pt/TiO_2 AMOX catalyst sample, 500 ppm NH_3 , 5 vol.% H_2O , 10 vol.% O_2 , and balance N_2 , with a total flow of 400 NmL/min.

Figure 5: Comparison of NH₃, NO, NO₂, N₂O, and N₂ outlet concentrations over the Cu-Beta catalyst, based on the experimental data (symbols) and the model fit for A) NH₃ oxidation (578 ppm NH₃), B) NO oxidation (470 ppm NO), C) NO₂ decomposition (463 ppm NO₂), D) standard SCR (563 ppm NH₃, 474 ppm NO), E) slow SCR (580 ppm NH₃, 497 ppm NO₂), and F) fast SCR (571 ppm NH₃, 236 ppm NO, 252 ppm NO₂). Values for N₂ were calculated from the N-balance. Operating conditions: 20 mg of 3.5 wt.% Cu-Beta SCR catalyst sample, 100 mg SiC, 5 vol.% H₂O, 10 vol.% O₂, and balance N₂, with a total flow of 1000 NmL/min. Activity measurements for ≤225°C were made with 40 mg catalyst and 200 mg SiC. This results in two points for 225°C (20 mg and 40 mg catalyst).

Figure 6: Simulation of the NO_x conversion and the corresponding weighting of x_{LT} and x_{HT} under standard SCR conditions ($NO_2/NO_x = 0$). Operating conditions: 20 mg of 3.5 wt.% Cu-Beta SCR catalyst sample, 600 ppm NH₃, 500 ppm NO, 5 vol.% H₂O, 10 vol.% O₂, and balance N₂, with a total flow of 1000 NmL/min.

Figure 7: NH₃ oxidation over the SL-AMOX, SL-SCR, SML, and DL ammonia slip catalysts. Solid symbols are the outlet concentrations measured during the activity measurements, while the solid lines are the simulated outlet concentrations using the monolith model. Values for N₂ were calculated from the N-balance. Operating conditions: 200 ppm NH₃, 4 vol.% H₂O, 12 vol.% O₂, and balance N₂, with a GHSV of 250,000 hr⁻¹ (total gas flow of 18,200 NL/hr and monolith volume of 0.073 L).

Table 5: ASC composition, effective diffusivity (expressed as mean pore diameter) and emissions at minimum objective function (eq. 24). Operating conditions: 300°C, 200 ppm NH₃, 4 vol.% H₂O, 12 vol.% O₂, balance N₂, with GHSV 250,000 hr⁻¹ (total gas flow of 18,200 NL/hr and monolith volume of 0.073 L). SL-AMOX: single layer AMOX catalyst ($\frac{AMOX}{AMOX}$); SL-SCR: single layer SCR catalyst ($\frac{SCR}{SCR}$); DL: dual layer catalyst ($\frac{SCR}{AMOX}$); IDL: inverse dual layer ($\frac{AMOX}{SCR}$); HDL-S: hybrid dual layer with SCR top layer ($\frac{SCR}{AMOX+SCR}$); IHDL-S: inverse hybrid dual layer with SCR bottom ($\frac{AMOX+SCR}{SCR}$); HDL-A: hybrid dual layer with AMOX top layer ($\frac{AMOX}{AMOX+SCR}$); IHDL-A: inverse hybrid dual layer with AMOX bottom ($\frac{AMOX+SCR}{AMOX}$); SML: single mixed layer ($\frac{AMOX+SCR}{AMOX+SCR}$); DML: dual mixed layer ($\frac{AMOX+SCR}{AMOX+SCR}$). Refer to Figure 2 for further details.

Configuration	Obj. Func.	Top layer					Bottom layer					Total			Emissions		
		<i>d</i> _{pore} nm	AMOX g/L	Pt Wt.%	Pt mg _{Pt} /L	SCR g/L	<i>d</i> _{pore} nm	AMOX g/L	Pt Wt.%	Pt mg _{Pt} /L	SCR g/L	AMOX g/L	SCR g/L	Pt mg _{Pt} /L	NH ₃ ppm	NO _x ppm	2*N ₂ O ppm
DML	51.4	189	1.0	3.5	35	16	197	1.4	1.3	18	177	2.4	193.0	53	16.9	14.3	20.2
HDL-AMOX	51.5	112	1.2	2.7	32	-	195	1.0	2.9	29	175	2.0	197.0	61	16.6	14.8	20.2
IHDL-SCR	51.6	200	1.0	6.1	61	49	200	-	-	-	140	1.0	200.0	61	16.3	14.0	21.3
IDL	54.0	200	1.0	6.1	61	-	200	-	-	-	200	1.1	200.0	61	12.2	16.6	25.2
HDL-SCR	54.8	194	-	-	-	2	200	1.0	6.1	61	160	1.0	162.0	61	27.3	11.0	16.4
SML	56.3	-	-	-	-	-	187	3.2	1.7	54	177	3.2	177.0	54	30.9	10.5	15.0
IHDL-AMOX	59.8	163	2.0	2.7	54	103	38	1.0	0.3	3	-	3.0	103.0	57	23.8	14.8	21.1
DL	75.2	200	-	-	-	81	200	1.0	6.0	61	-	1.3	95.0	61	38.1	13.3	23.8
SL-AMOX	119.8	-	-	-	-	-	200	1.0	6.1	61	-	1.0	-	61	18.7	52.5	48.6
SL-SCR	191.5	-	-	-	-	-	200	-	-	-	200	-	200.0	-	191.5	0.0	0.0

Figure 8: Pareto fronts generated for the ten ammonia slip catalyst configurations investigated. Operating conditions: 300°C, 200 ppm NH_3 , 4 vol.% H_2O , 12 vol.% O_2 , balance N_2 , with GHSV 250,000 hr^{-1} (total gas flow of 18,200 NL/hr and monolith volume of 0.073 L). SL-AMOX: single layer AMOX catalyst ($\frac{\text{AMOX}}{\text{AMOX}}$); SL-SCR: single layer SCR catalyst ($\frac{\text{SCR}}{\text{SCR}}$); DL: dual layer catalyst ($\frac{\text{SCR}}{\text{AMOX}}$); IDL: inverse dual layer ($\frac{\text{AMOX}}{\text{SCR}}$); HDL-S: hybrid dual layer with SCR top layer ($\frac{\text{SCR}}{\text{AMOX+SCR}}$); IHDL-S: inverse hybrid dual layer with SCR bottom ($\frac{\text{AMOX+SCR}}{\text{SCR}}$); HDL-A: hybrid dual layer with AMOX top layer ($\frac{\text{AMOX}}{\text{AMOX+SCR}}$); IHDL-A: inverse hybrid dual layer with AMOX bottom ($\frac{\text{AMOX+SCR}}{\text{AMOX}}$); SML: single mixed layer ($\frac{\text{AMOX+SCR}}{\text{AMOX+SCR}}$); DML: dual mixed layer ($\frac{\text{AMOX+SCR}}{\text{AMOX+SCR}}$). Refer to Figure 2 for further details.

Feltkode ændret

Supporting Information

The performed multi-objective optimization will now be described in more detail. As illustrated by the figure below, the process begins with a set of initial guesses, either randomly adhering to selected constraints, or based on user defined inputs. The parameter set consists of 50 initial guesses multiplied by the number of parameters (n_{param}) being varied, to account for the increase in possible solutions with the increase in parameters for the more complex configurations. The genetic algorithm generates a new collection of parameter values based on a score of according to the objective function (eq. 24). Generally, the best performing parameter sets are selected as initial guesses for the next iteration, but some poorer performing parameter sets may also be selected to diversify the optimization. The generated parameter sets may be either: 1) elite, which are replicates of the most fit parameter sets, 2) mutation, which are created by introducing random changes to a single parameter set, and 3) crossover, which are created by combining the vectors of a pair of initial guesses. Through the successive iterations, the parameter sets evolve toward a set of optimal solutions. This loop of the algorithm is repeated until a stopping criteria is met, such as when a maximum number of iterations is reached or when the relative change in the objective function decreases below a set tolerance. In this study a maximum number of 10 iterations (n_{gen}) was used as the stopping criteria. The total number of simulations performed for a configuration is therefore $50 \times n_{param} \times n_{gen}$, including the replicates from previous generations. The Pareto fronts resulting from the final set of optimal solutions were used to evaluate the sensitivity of the ASC performance to the possible ASC configurations.

Figure 9: Flow chart for the genetic algorithm used to optimize the multi-objective ammonia slip catalyst design.