Experimental and theoretical study of NH$_3$ adsorption and desorption over a Cu-chabazite NH$_3$-SCR catalyst

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Received: 28.03.2017 • Accepted/Published Online: 06.08.2018 • Final Version: 06.12.2018

Abstract: NH$_3$ adsorption and desorption behavior of a commercial Cu-chabazite (CHA) NH$_3$ selective catalytic reduction (NH$_3$-SCR) catalyst was studied in the presence and absence of H$_2$O. NH$_3$ uptake values at various adsorption temperatures were obtained during various steps of the adsorption and temperature-programmed desorption (TPD) experiments. Total NH$_3$ uptake decreased from 4.6 to 1.6 g NH$_3$/L catalyst when the adsorption temperature was increased from 50 to 300 °C. Three major adsorption sites for NH$_3$ adsorption could be identified and quantified using TPD experiments, namely loosely, moderately, and strongly bound NH$_3$ with peak centers at around 147, 266, and 447 °C. The total NH$_3$ uptake was significantly affected by the presence of H$_2$O in the feed. This resulted in a significant uptake loss (nearly 60%) for the loosely bound NH$_3$. Three single-site and one three-site model were developed and compared in terms of NH$_3$ uptake and release. The effects of site density values and thermodynamic restrictions in one-site models were investigated. The model using site density values obtained during the TPD phase resulted in the best fit among one-site models. The three-site model, which uses site density values obtained using dry adsorption of NH$_3$, best represented the experimental data.

Key words: Copper, chabazite, monolith, NH$_3$, adsorption, storage, desorption, model, kinetics

1. Introduction

NOx abatement using NH$_3$ selective catalytic reduction (NH$_3$-SCR) technology is widely used for aftertreatment of diesel vehicles. Cu-zeolites with chabazite structures have attracted both academic and industrial interest due to their high NOx conversion at a desirable temperature range and good hydrothermal resistance.$^1$–$^4$ The NH$_3$-SCR reaction over Cu-zeolites is generally described by a complicated mechanism in which the adsorbed NH$_3$ reacts with adsorbed nitrite or nitrate species formed in the presence of NO or NO$_2$ to yield N$_2$ and H$_2$O.$^5$–$^6$

Modeling of catalytic converters is necessary for both design and control of aftertreatment systems and development of a detailed kinetic model of an SCR reactor requires the understanding of the adsorption and desorption behavior of NH$_3$ since the NH$_3$ concentration on the catalyst surface could significantly increase or decrease deNOx activity, particularly in transient operations.$^7$–$^{12}$ On a Cu-chabazite catalyst surface, the NH$_3$ uptake mechanism is complex. Active Cu cores in zeolites such as monomeric Cu$^{2+}$-OH$^6$,$^{13}$ or dimeric...
(mono(μ-oxo)dicopper\textsuperscript{14} or bis(μ-oxo)dicopper\textsuperscript{15,16} and Brønsted sites\textsuperscript{17−20} were proposed as uptake sites. Weakly bound physisorption sites were also reported.\textsuperscript{10} An accurate knowledge of the active site density for NH\textsubscript{3} uptake is necessary to extract realistic reaction rate parameters (activation energy and preexponential factor) by fitting experimental reactor exit composition data to kinetic models. NH\textsubscript{3} uptake models in the literature often use active site densities that are optimized along with the reaction rate parameters,\textsuperscript{9−11,21} which not only increases optimization time but may also result in the inaccurate description of the kinetic processes. Moreover, except for a limited number of reports,\textsuperscript{22,23} the effect of H\textsubscript{2}O on the adsorption of NH\textsubscript{3} is usually neglected in the SCR kinetics literature although it is well known that Cu-zeolites can store a significant amount of H\textsubscript{2}O. This behavior could affect the SCR kinetics especially during the cold-start of the vehicle. H\textsubscript{2}O adsorption is usually accounted for by lumping this effect into the kinetic parameters for NH\textsubscript{3} adsorption/desorption in order not to further complicate the models. Although the multisite approach with lumped parameters seems to result in fairly good representation of the general behavior of NH\textsubscript{3} adsorption/TPD data,\textsuperscript{10} the prediction of the NH\textsubscript{3} desorption behavior during isothermal desorption and TPD steps of the experiments could possibly be improved by employing more realistic site density values obtained using dry NH\textsubscript{3} uptake experiments. However, no such studies exist.

In this study, NH\textsubscript{3} uptake amounts of a commercial Cu-CHA catalyst at various temperatures in the presence and absence of H\textsubscript{2}O were measured. Amounts of NH\textsubscript{3} stored at various adsorption temperatures ranging from 50 to 300 °C were determined. The release of NH\textsubscript{3} from the surface was investigated by TPD experiments to assess the nature of active sites. Three single-site and one multisite model, which used the site density values from the experiments without H\textsubscript{2}O presence in the feed, were developed and compared in terms of NH\textsubscript{3} adsorption and TPD.

2. Results and discussion
2.1. Determination of the site density for Models 1–3

Figure 1 illustrates the variation of the measured NH\textsubscript{3} uptake during the adsorption, isothermal desorption, and TPD phases of the experiments as a function of the adsorption temperature. The uptakes associated with the adsorption and isothermal desorption phases decreased with increasing adsorption temperature. Total NH\textsubscript{3} uptake measured during the adsorption phase at 50 °C was 2.4 and 4.6 g/L with and without the presence of H\textsubscript{2}O in the feed, respectively. This indicates that H\textsubscript{2}O blocks some of the adsorption sites for NH\textsubscript{3}. At 50 °C, most of the blockage was associated with the loosely bound NH\textsubscript{3}, i.e. NH\textsubscript{3} desorbed in the isothermal desorption phase, as illustrated in Figures 1a and 1b. The blockage corresponded to 58% of the loosely bound sites. Above 50 °C, NH\textsubscript{3} uptake amounts were very similar for both dry and wet experiments in all of the experimental phases. The value obtained during dry adsorption (i.e. 4.6 g/L) at 50 °C was used as the site density parameter for Models 2 and 3.

If one considers a material balance for H\textsubscript{3} during the whole experiment, summation of the uptakes measured during the isothermal desorption and TPD phases should be equal to the total uptake measured...
The variations of the NH$_3$ uptakes measured during the adsorption, isothermal desorption, and TPD phases as a function of the adsorption temperature for (a) dry and (b) wet feed during the adsorption phase.

during the adsorption phase. In all of our experiments, the aforementioned material balance held with a maximum error of 7%, indicating the consistency of the results.

2.2. Determination of the site densities for Model 4

In order to elucidate the distribution of the surface site density among various sites of Model 4, an analysis of the TPD curves at different adsorption temperatures was carried out. The variations of TPD curves obtained using dry adsorption feeds at different adsorption temperatures are presented in Figure 2. The TPD curve observed for the adsorption at 50 °C (Figure 2a) shows three major peaks with peak centers at 147, 266, and 446 °C that could easily be assigned to the three different adsorption sites for NH$_3$. As the adsorption temperature increased to 150 °C, the first peak centered at around 147 °C disappeared (Figure 2b). This implies that NH$_3$ stored at this site is desorbed either during the adsorption or isothermal desorption phases when the adsorption is carried out at temperatures ≥150 °C. The aforementioned site is associated with site S3 in Model 4 and the site density of S3 was calculated by subtracting the uptake value obtained from the TPD phase at 50 °C (i.e. the site density parameter for Models 2 and 3) from that of 150 °C and adding the uptake value obtained during the isothermal desorption phase at 50 °C (i.e. A$_{S3}$ = 2.4 g/L). TPD curves obtained for adsorption at 150 and 200 °C show two peaks associated with different NH$_3$ uptake sites (Figures 2b and 2c), whereas for the adsorption at 300 °C only one clear peak was observed during the TPD (Figure 2d). We therefore assigned the NH$_3$ uptake associated with this peak to site S2 of Model 4 since S2 is associated with adsorption at higher temperatures (i.e. A$_{S2}$ = 0.7 g/L). Site density of S1 of Model 4 was then obtained by subtracting the site density of S2 and S3 from the total uptake value obtained during the adsorption phase at 50 °C (i.e. A$_{S1}$ = 1.5 g/L).

Figures 3a–3d illustrate the TPD curves for adsorption at different temperatures in wet feed. The data are very similar to those of the dry feed. Slightly lower uptake values were obtained, as previously discussed.

2.3. Modeling of NH$_3$ adsorption and desorption

Figure 4 shows a comparison of the data from the TPD experiment and the single-site kinetic models (Models 1–3). In the experiment, the feed to the reactor contained 500 ppm of NH$_3$ at 100 °C in the presence of 5%
Effect of adsorption temperature on the chemisorption of NH$_3$ for dry adsorption feed at different adsorption temperatures: (a) 50 °C, (b) 150 °C, (c) 200 °C, (d) 300 °C.

H$_2$O and 10% CO$_2$, during which adsorption breakthrough was observed. This was followed by an isothermal desorption period where the NH$_3$ feed was terminated and a temperature ramp of 10 °C/min was introduced again in the presence of 5% H$_2$O and 10% CO$_2$. Two NH$_3$ desorption peaks with peak centers at 300 and 420 °C were observed. All single-site models represented fairly well the general behavior of the TPD experiment. However, the models were not very successful in simulating the desorption of the loosely bound NH$_3$ in the isothermal desorption phases and all models underpredicted the outlet NH$_3$ concentration. In the TPD phase, all single-site models resulted in a broad desorption peak while overpredicting the NH$_3$ desorption in the 100–320 °C region where moderately bound NH$_3$ desorbed. This can be attributed to the relatively poor description of the active surface using only one site. The effect of the site-density value in the models was significant. Fits in the TPD phases were improved using the site-density value obtained during the TPD phase (Model 2) instead of the one obtained during the adsorption phase (Model 1). Employing a thermodynamic constraint on the kinetic model (Model 3) did not result in a further improvement of the fit.

Figure 5 shows the kinetic fit from the three-site kinetic model (Model 4) and the data from the experiment are illustrated in Figure 4. The three-site model gave an excellent representation of all three phases of the TPD experiment. As compared to single-site models (Models 1–3), significant improvements were observed in representing both the isothermal desorption and TPD phases. Curvature of the adsorption breakthrough was also better represented with the three-site model.
Figure 3. Effect of adsorption temperature on the chemisorption of NH₃ for the wet adsorption feed at different adsorption temperatures: (a) 50 °C, (b) 150 °C, (c) 200 °C, (d) 300 °C.

Figure 4. Experiment and single-site kinetic models for NH₃ adsorption and TPD.

Figure 5. Experiment and multisite kinetic model for NH₃ adsorption and TPD.

As can be observed from Figures 4 and 5, the TPD curve shows some differences in the relative intensities of the desorption peaks for moderately (around 300 °C) and strongly (around 420 °C) bound NH₃ as compared
to the relative intensities from the TPD curves illustrated in Figures 2 and 3, i.e. where no H\textsubscript{2}O was present during the isothermal desorption or the TPD phases. The intensity of the peak around 300 °C was lower than the peak around 420 °C when H\textsubscript{2}O was present during the whole experiment in contrast to the higher intensity of the 420 °C peak as compared to the 300 °C peak when a dry stream was used during the TPD phase. This behavior was also successfully captured by the three-site model. This change in the relative intensities could very well be associated again with the blockage of NH\textsubscript{3} uptake sites by H\textsubscript{2}O and also by the spill-over of the moderately bound NH\textsubscript{3} (on S1) to lower energy sites and desorption from these sites (on S3). Figure 6 shows the TPD curve of H\textsubscript{2}O obtained after the adsorption of H\textsubscript{2}O (5\% in N\textsubscript{2} balance) on the catalyst at 200 °C. The TPD curve clearly shows the desorption of relatively strongly bound H\textsubscript{2}O centered around 350 °C whose adsorption would undoubtedly affect NH\textsubscript{3} adsorption as previously discussed. Although the three-site model presented in this study does not involve any H\textsubscript{2}O adsorption-desorption reaction, the behavior originating from H\textsubscript{2}O blockage was well represented by lumping the blockage/spill-over behavior in the fitted kinetic parameters.

Figure 7 illustrates the changes in the coverages of the adsorbed NH\textsubscript{3} species on three sites, namely S1-NH\textsubscript{3}, S2-NH\textsubscript{3}, and S3-NH\textsubscript{3}, throughout the adsorption/TPD experiment. According to Model 4, NH\textsubscript{3} covers all of the S1 sites and a portion of the S2 and S3 sites during the adsorption phase. The differences between the modeled coverages of S2 and S3 and their uptake capacities are associated with the adsorption of H\textsubscript{2}O on these sites. The effect of H\textsubscript{2}O adsorption is thus successfully lumped into the kinetic parameters since the model uses site density values obtained from the NH\textsubscript{3} adsorption experiments without H\textsubscript{2}O. As NH\textsubscript{3} feed was cut off around 5000 s the coverage of S1-NH\textsubscript{3} decreased to 0.8 and the coverage of S3-NH\textsubscript{3} diminished to zero in the isothermal desorption period where no desorption from S2 sites could be observed. This behavior is consistent with how the site densities of uptake sites were obtained and is also in agreement with the NH\textsubscript{3} uptake values obtained when H\textsubscript{2}O was present during the NH\textsubscript{3} adsorption experiments. As the temperature is increased in the TPD phase NH\textsubscript{3} started desorbing from S1 sites and desorption continued as the temperature was raised. The desorption from the S2 sites started around 300 °C and continued as the temperature was raised up to 570 °C in accordance with the higher activation energy fitted for S2 as compared to S1 and S3.

\[\text{Figure 6. Measured H}_2\text{O concentration during H}_2\text{O TPD experiment.}\]

\[\text{Figure 7. Calculated coverages at the last volume element in Model 4.}\]

NH\textsubscript{3} uptake values for a Cu-CHA catalyst were obtained for dry and wet feeds at various adsorption temperatures. Uptake decreased with increasing adsorption temperature. H\textsubscript{2}O blockage on NH\textsubscript{3} uptake sites was elucidated. Fifty-eight percent of the sites associated with loosely bound NH\textsubscript{3} were blocked when H\textsubscript{2}O was
present in the adsorption stream. Further site blockage by H$_2$O was also observable when H$_2$O was present during isothermal desorption and TPD phases as well, which resulted in the change of the relative intensities of the moderately and strongly bound NH$_3$ as compared to the experiments carried out without H$_2$O during these phases. Uptake and release of NH$_3$ from Cu-CHA were successfully modeled using various approaches. Single-site approaches gave fairly good fits while failing to reproduce the isothermal desorption and the initial part of TPD phases. A three-site model was developed, which uses the site density values obtained during dry adsorption of NH$_3$. Site densities of the three uptake sites were obtained by performing adsorption experiments at different adsorption experiments. The three-site model was successful in reproducing all of the phases of the adsorption/TPD experiment and the coverage effects originating from H$_2$O presence. This model represents a very promising starting point for the detailed modeling of the whole NH$_3$-SCR process.

3. Experimental

3.1. Experimental

The catalyst used in this study was obtained from a commercial supplier in the form of a cordierite monolith (300 cpsi – 5 mils). A cylindrical core with a length of 2.2 cm and a diameter of 1.9 cm was cut from the monolith and was used in the runs.

The experiments were carried out in a synthetic gas bench (Figure 8). In a typical run, the monolith was first wrapped with a ceramic fiber paper and then loaded in a quartz reactor and placed in the isothermal zone of an electric tubular furnace (Thermo Scientific Lindberg Blue M). The reaction temperature was monitored using a J-type thermocouple placed 0.5 cm upstream of the catalyst. NH$_3$, CO$_2$, and N$_2$ were dosed using mass flow controllers (Brooks Instruments), whereas H$_2$O was dosed using a peristaltic pump (Gilson Minipuls 3). All lines before and after the reactor were heated to 190 °C. The species concentrations at the outlet of the reactor were continuously monitored using a FTIR spectrometer (MKS Multigas 2030). Initially, the catalyst was degreened at 600 °C using 5% H$_2$O, 8% O$_2$, and 10% CO$_2$ in N$_2$ balance for 4 h. After all of the experiments, the catalyst was exposed to 8% O$_2$ in N$_2$ balance at 600 °C for 30 min to clean the surface of any N-containing residues. All the gas grades used were 5.0 or above.

TPD experiments consisted of adsorption, isothermal desorption, and TPD phases, as illustrated in Figure 9. Table 1 summarizes the experiments carried out in this study. In a typical experiment, NH$_3$ concentration was first checked using FTIR via a bypass line followed by the introduction of NH$_3$-containing feed to the reactor (illustrated by the blue dashed line), which evidently resulted in an adsorption breakthrough curve. Once adsorption was complete, NH$_3$ addition to the feed was stopped (illustrated by the green dashed line) and the isothermal desorption profile of weakly bound NH$_3$ was obtained. Once the weakly bound NH$_3$ was desorbed, a temperature ramp was started with a rate of 10 °C/min. Experiments were carried out at different adsorption temperatures (50–300 °C) using 500 ppm NH$_3$ followed by an isothermal desorption phase, which was followed by the TPD phase. Three types of TPD experiments were carried out. In the first series, a dry stream was used for all of the three phases. The second series consisted of a wet stream (5% H$_2$O) during the adsorption phase and a dry stream during the isothermal desorption and TPD phases. These two types of experiments were used to obtain the NH$_3$ uptake values. For the third type of experiment, a wet stream (5% H$_2$O) was utilized during all of the three phases (here the adsorption was carried out at 100 °C) and this experiment was used for kinetic modeling. Uptake values and the TPD peak center temperatures are reported with standard deviations of less than 3% of the actual value and less than 1.5 °C, respectively.
3.2. The reactor model

The kinetic modeling was performed using GT-SUITE, version 2017. Material balances are provided below. Momentum and energy balances were also solved. All channels were assumed to be uniform and the catalyst monolith length was discretized into 10 grid points. Accumulation in the bulk gas phase was neglected due to
Table 1. Summary of experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Adsorption &amp; isothermal desorption temperature</th>
<th>H₂O concentration in the feed</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Adsorption Isothermal desorption TPD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>50 °C</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>2</td>
<td>50 °C</td>
<td>5%</td>
<td>0%</td>
</tr>
<tr>
<td>3</td>
<td>150 °C</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>4</td>
<td>150 °C</td>
<td>5%</td>
<td>0%</td>
</tr>
<tr>
<td>5</td>
<td>200 °C</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>6</td>
<td>200 °C</td>
<td>5%</td>
<td>0%</td>
</tr>
<tr>
<td>7</td>
<td>300 °C</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>8</td>
<td>300 °C</td>
<td>5%</td>
<td>0%</td>
</tr>
<tr>
<td>9</td>
<td>100 °C</td>
<td>5%</td>
<td>5%</td>
</tr>
</tbody>
</table>

Adsorption x°C: The uptake value obtained during the adsorption phase at x °C.
Isodes x°C: The uptake value obtained during the isothermal desorption after the adsorption phase at x °C.
TPD x°C: The uptake value obtained during the TPD after the adsorption phase at x °C.

the very low residence time used. The film model was used for the external mass transfer from the bulk fluid to the surface and a washcoat diffusion model was included for the mass transfer within the washcoat.

The main material balance for the gas phase is:

\[ \varepsilon \rho_g \frac{\partial \omega_{g,i}}{\partial z} = k_{m,i} G (\omega_{w,i} - \omega_{g,i}) \] (1)

The material balance for the external mass transfer film gives:

\[ k_{m,i} G (\omega_{w,i} - \omega_{g,i}) = R_i, \] (2)

with

\[ R_i = M_i \sum_j s_{ij} a_j r_j. \] (3)
The material balance for the washcoat is:

\[ f_{wc} \rho_s D_{e,i} \frac{\partial^2 \omega_i}{\partial x^2} + R_i = 0, \quad (4) \]

with

\[ -f_{wc} \rho_s D_{e,i} \frac{\partial \omega_i}{\partial x} = k_{m,i} S(\omega_{w,i} - \omega_{g,i}) \text{ at } x = 0 \quad (5) \]

and

\[ \frac{\partial \omega_i}{\partial x} = 0 \text{ at } x = \delta, \text{ with } \delta = \frac{f_{wc}}{G}. \]

The surface coverages are given by:

\[ A_k \frac{d\theta_k}{dt} = \sum_j \sigma_{kj} a_j r_j. \quad (6) \]

### 3.3. Kinetic models

Several kinetic models were developed for the adsorption of NH\(_3\). The Arrhenius equation was used in all of them to account for the temperature dependency of the turnover rate constant, \( k_i \):

\[ k_j = A_j e^{-\frac{E_{A,i}}{RT}}, \quad (7) \]

where \( A_j \) is the preexponential factor and \( E_A \) is the activation energy. A coverage-dependent activation energy function was used to describe the desorption of NH\(_3\):

\[ E_{A,j} = E_{A,j,0}(1 - a\theta_{NH_3S}). \quad (8) \]

Adsorption was assumed to be nonactivated. All reactions and rate equations used in the models are presented in Table 2. Models 1–3 are conventional 1-site models in which Eqs. (7) and (8) were used in Reaction 2. Model 1 and Model 2 use site density values obtained from the NH\(_3\) adsorption and TPD phases (adsorption at 50 °C), respectively. The preexponential factors and activation energy values were optimized using a genetic algorithm by keeping the aforementioned site-density values constant.

In Model 3, the site density was the same as in Model 2 but this time an estimated change in entropy\(^{22}\) was used as a constraint during the optimization of the rate parameters:

\[ \Delta S = R \ln \left( \frac{A_{i,adsorption}}{A_{i,desorption}} \right). \quad (9) \]

Entropy loss due to the adsorption was calculated as –168 J/mol K using:

\[ S = R \ln(q) + RT \frac{d(\ln(q))}{dT}, \quad (10) \]

where \( q \) is the partition function, calculated using the rotational partition function, \( q_{rot} \), for a nonlinear molecule:

\[ q_{rot} = \frac{8\pi^2 \sqrt{8\pi^3 I_x I_y I_z(k_BT)^{3/2}}}{\sigma_r h^2}. \quad (11) \]
Table 2. Reactions and rate expressions used in this study.

<table>
<thead>
<tr>
<th>Reaction number</th>
<th>Reaction</th>
<th>Reaction rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$NH_3 + S \rightarrow S - NH_3$</td>
<td>$r_1 = k_1 f C_{NH_3} \theta_S$</td>
</tr>
<tr>
<td>2</td>
<td>$S - NH_3 \rightarrow NH_3 + S$</td>
<td>$r_2 = k_2 \theta_{S-NH_3}$</td>
</tr>
<tr>
<td>3</td>
<td>$NH_3 + S1 \rightarrow S1 - NH_3$</td>
<td>$r_3 = k_2 f C_{NH_3} \theta_{S1}$</td>
</tr>
<tr>
<td>4</td>
<td>$S1 - NH_3 \rightarrow NH_3 + S1$</td>
<td>$r_4 = k_2 \theta_{S1-NH_3}$</td>
</tr>
<tr>
<td>5</td>
<td>$NH_3 + S2 \rightarrow S1 - NH_3$</td>
<td>$r_5 = k_3 f C_{NH_3} \theta_{S2}$</td>
</tr>
<tr>
<td>6</td>
<td>$S2 - NH_3 \rightarrow NH_3 + S2$</td>
<td>$r_6 = k_3 \theta_{S2-NH_3}$</td>
</tr>
<tr>
<td>7</td>
<td>$NH_3 + S3 \rightarrow S3 - NH_3$</td>
<td>$r_7 = k_4 f C_{NH_3} \theta_{S3}$</td>
</tr>
<tr>
<td>8</td>
<td>$S3 - NH_3 \rightarrow NH_3 + S3$</td>
<td>$r_8 = k_4 \theta_{S3-NH_3}$</td>
</tr>
</tbody>
</table>

$NH_3$ was assumed to adsorb as a localized species; thus, translational and one-third of the rotational entropy was assumed to be lost. The vibrational partition function was found close to unity; therefore, it was neglected.

Model 4 is a 3-site model consisting of Reactions 3–8 in Table 2 where both Cu and Brönsted sites of the catalyst were lumped into two sites, S1 and S2, i.e. both sites have contributions from both Cu and Brönsted sites. S1 is the main uptake site for the adsorption at moderate temperatures and S2 is the uptake site for higher temperatures. S3 is the uptake site for the physisorbed $NH_3$. In Model 4, Eq. (8) was used only for Reaction 4. No thermodynamic constraint was used for estimation of the rate parameters of Model 4. The estimation of the site density values for different sites in Model 4 was discussed in Section 2.2. Coverage-dependent activation energy was not used for Reactions 6 and 8 so as to not further complicate the model.

Nomenclature

- $a_j$: Active site density for reaction $j$ (mol/m$^3$ catalyst)
- $A_k$: Active site density for coverage $k$ (mol/m$^3$ catalyst)
- $A_i$: Preexponential factor for reaction $j$
- $C_i$: Intraporous concentration of species $i$ (mol/m$^3$)
- $D_{e,i}$: Effective diffusivity for component $i$ (m$^2$/s)
- $E_{A,i}$: Activation energy for reaction $j$ (J/mol)
- $E_{A,1.0}$: Activation energy for reaction $j$ at zero coverage (J/mol)
- $f_{wc}$: Solid fraction of washcoat
- $G$: Surface area per reactor volume (m$^{-1}$)
- $h$: Planck’s constant (J s)
- $I_i$: Rotational moment of inertia in direction $i$, with $i = x, y, z$ (kg m$^2$)
- $k_B$: Boltzmann’s constant (J/K)
- $k_i$: Turnover rate constant for reaction $j$ (depends on rate expression)
- $k_{m,i}$: External mass transfer coefficient for species $i$ (kg/m$^2$ s)
- $M_i$: Molecular weight of species $i$ (kg/mol)
- $r_j$: Reaction rate per active site for reaction $j$ (mol/s mol)
- $q$: Partition function
- $q_{rot}$: Partition function for rotation
- $R$: Gas constant (J/mol K)
- $R_i$: Species mass rate for generation or consumption (kg/m$^3$ s)
- $s_{ij}$: Stoichiometric coefficient of species $i$ for reaction $j$
\[ S \] Entropy (J/mol K)
\[ \Delta S \] Entropy change due to adsorption (J/mol K)
\[ v \] Interstitial velocity (m/s)

**Greek letters**
- \( \alpha \): Coverage dependence
- \( \delta \): Washcoat thickness (m)
- \( \varepsilon \): Void fraction of reactor
- \( \rho_g \): Density of bulk gas in reactor channels (kg/m\(^3\))
- \( \omega_i \): Intraporous mass fraction of species i
- \( \omega_{g,i} \): Mass fraction of species i in the bulk
- \( \omega_{w,i} \): Mass fraction of species i in the gas/solid interface
- \( \theta_k \): Surface coverage of species k
- \( \sigma_{kj} \): Stoichiometric coefficient of coverage k in reaction j
- \( \sigma_r \): Symmetry number

**Acknowledgment**

We acknowledge the financial support from Ford Otomotiv San. AŞ.

**References**