Article

Simple Rate Expression for Catalyzed Ammonia Decomposition for Fuel Cells

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Abstract: This paper examines NH₃ decomposition rates based on a literature-proven six-step elementary catalytic (Ni-BaZrO₃) mechanism valid for 1 × 10⁵ Pa pressure in a 650–950 K range. The rates are generated using a hypothetical continuous stirred tank catalytic reactor model running the literature mechanism. Excellent correlations are then obtained by fitting these rates to a simple overall kinetic expression based on an assumed slow step, with the remaining steps in fast pseudo-equilibria. The robust overall simple rate expression is then successfully demonstrated in various packed bed reactor applications. This expression facilitates engineering calculations without the need for a complex, detailed mechanism solver package. The methodology used in this work is independent of the choice of catalyst. It relies on the availability of a previously published and validated elementary reaction mechanism.

Keywords: catalyst; ammonia; mechanism; decomposition; CSTR; packed bed

1. Background

Motivated by global warming, the worldwide movement to decarbonize national economies continues to grow. Fuels high in hydrogen content (e.g., CH₄ or pure H₂) are preferred. Compressed natural gas for transportation fleets is well known. The popularity and performance of battery-powered pure electric vehicles are growing despite limited charging stations and relatively long battery recharging times.

As a non-carbon fuel, liquid NH₃ is attracting increasing attention [1]. It combines the advantages of easy storage and transport without producing greenhouse gases. Anhydrous liquid NH₃ is typically stored at 9.6 × 10⁵ Pa absolute at room temperature. “Green” NH₃ can be catalytically produced from N₂ and H₂ using solar power [2]. Ammonia as a H₂ source is gaining considerable attention [3].

While direct NH₃ combustion produces H₂O and N₂ as major products, temperatures can easily exceed 1000 K, resulting in pollutant nitrogen oxides [4]. To avoid these temperatures, fuel cells are preferred for the oxidation of the H₂ from NH₃ decomposition [2,5]. Ammonia-powered fuel cells are now being tested for freight-hauling vehicles, including large trucks [6] and locomotives [7].

Production of H₂ from NH₃ can be accomplished in various ways, including catalytic decomposition from either gaseous or solution NH₃ [3]. Various metals (e.g., Ru, Ir, Ni, and Rh) and supports have been investigated as catalysts for the decomposition of gaseous NH₃ [3,8]. While Ru shows excellent activity, its high cost and limited availability make Ni more attractive [8]. An alternative approach is the decomposition of NH₃ in solution using electrocatalysts [3].

In the typical ammonia-powered fuel cell, H₂ produced from gaseous NH₃ decomposition yields protons at the anode, thus releasing electrons into the external load circuit. The protons diffuse across a membrane to the cathode, where they react with O₂ (typically from air) to form H₂O vapor, and the electron circuit is completed. In ceramic fuel cells, temperatures can exceed 1000 K due to H₂ oxidation exothermicity. At this level, the
kinetics of the endothermic NH₃ decomposition are sufficiently fast that NH₃ can directly feed the fuel cell [9]. However, the risk of NOₓ formation still exists. Therefore, care is needed for NH₃ decomposition catalyst and fuel cell designs to avoid these temperatures.

In this paper, a simple kinetic engineering model is developed for NH₃ decomposition over a Ni-BaZrO₃ catalyst. This model is calibrated over a relevant temperature range using reaction rates obtained from a detailed published elementary reaction mechanism [9]. The performance of this model is then compared to that of the detailed mechanism in simulations of packed bed (plug flow PBR) ideal adiabatic reactors. The utility of the engineering model is further demonstrated with simulations of PBRs with heat transfer and H₂ diffusion. This simple model is intended to facilitate quick engineering calculations and screening studies for fuel cell design.

It should be noted that the purpose of this paper is the demonstration of a calculation methodology assuming the availability of a proven, detailed reaction mechanism. Catalyst choice, design, and effectiveness are beyond the scope of this work.

2. Equilibrium

Ammonia decomposition \([NH₃ \rightarrow 0.5N₂ + 1.5H₂]\) is endothermic \((\Delta H^{\text{298K}} = 45,900 \text{ J})\) and becomes thermodynamically favorable above approximately 450 K (at \(1 \times 10^5 \text{ Pa}\)). Figure 1 shows the equilibrium conversion over a wide temperature range at \(1 \times 10^5 \text{ Pa}\) pressure for pure NH₃ feed, with complete conversion above 650 K. The calculation uses an online equilibrium calculator [10], with results consistent with published species thermodynamic properties [11]. The temperature range of this study is 650–950 K at \(1 \times 10^5 \text{ Pa}\) pressure. Therefore, the decomposition is not thermodynamically limited under the conditions of this study.

![Equilibrium NH₃ conversion for pure NH₃ feed at 1 x 10^5 Pa pressure. Calculation based on NASA CEA equilibrium code [10].](image_url)

Figure 1. Equilibrium NH₃ conversion for pure NH₃ feed at \(1 \times 10^5 \text{ Pa}\) pressure. Calculation based on NASA CEA equilibrium code [10].

3. Kinetics and Mechanism

A common mechanism in the literature [9] for NH₃ decomposition on a Ni-based catalyst consists of the following six elementary reversible steps:

1. \(NH₃ + S = NH₃·S\)

2. \(NH₃·S + S = NH₂·S + H·S\)
3. $\text{NH}_2 \cdot S + S = \text{NH} \cdot S + H \cdot S$

4. $\text{NH} \cdot S + S = \text{N} \cdot S + H \cdot S$

5. $\text{N} \cdot S + \text{N} \cdot S = \text{N}_2 + 2S$

6. $H \cdot S + H \cdot S = H_2 + 2S$

where $S$ represents an unoccupied catalytic site, and $\# \cdot S$ is an adsorbed species. Zhu et al. [9] validated this mechanism for a Ni-BaZrO$_3$ catalyst over $\sim$650–950 K range at $1 \times 10^5$ Pa pressure using experimental data from Okura et al. [8]. The kinetic parameters are presented there for both the forward and reverse steps. This eliminates the need for any estimates of thermodynamics for surface-adsorbed species that would be needed if kinetic parameters were provided for only the forward steps.

The entire mechanism is “thermodynamically consistent”. This means that accurate (thermodynamically) reaction equilibrium gas compositions ($\text{NH}_3$, $\text{N}_2$, and $\text{H}_2$) are achieved if a time-dependent (kinetic) ammonia decomposition PBR flow reactor simulation is carried out for a sufficiently long time. These kinetic parameters are used in this study as described below. This was demonstrated by Karakaya et al. [12] with an elementary catalytic mechanism for methane oxidative coupling.

A two-pronged strategy is used in the current study. In the first portion, simulations of catalyzed $\text{NH}_3$ decomposition are performed using continuously stirred tank reactor (CSTR, perfectly mixed) calculations together with the detailed mechanism shown above. These provide rates of $\text{NH}_3$ decomposition as functions of $\text{NH}_3$, $\text{H}_2$, and $\text{N}_2$ partial pressures. These rates are then used to calibrate a proposed single overall kinetic expression for $\text{NH}_3$ decomposition derived from a fast pseudo-equilibrium analysis applied to the detailed six-step mechanism shown above. In the second portion, the calibrated single kinetic rate expression is used in simple packed bed reactor (PBR, perfect plug flow) simulations to demonstrate its utility in engineering and screening calculations.

### 4. Simplified Overall Rate Expression

The six-step, detailed elementary reaction mechanism described above is authoritative for kinetic reactor simulations. However, such simulations require a computation package such as Detchem$^\text{®}$ [13]. It is often desirable to reduce such mechanisms to a simple kinetic rate expression for relatively quick engineering calculations. Such a reduction is applied here using the fast pseudo-equilibrium approach based on the Langmuir–Hinshelwood algorithm [14].

#### 4.1. Derivation by Langmuir–Hinshelwood Algorithm

The algorithm applied to the six-step mechanism begins with choosing a rate-determining (slow) step. The slow step is taken as effectively irreversible. The remaining steps are assumed to be in fast pseudo-equilibrium (FPE). Consider Step 5 to be the slow step, as recommended by Bell and Torrente-Murciano [15] for a Ni-based $\text{NH}_3$ decomposition catalyst:

$$-r_{\text{NH}_3} = r_{\text{slow}} \equiv r_5 = k_5C_{N \cdot S}^2$$  \hfill (1)

where $C_{j \cdot S}$ is the surface concentration of the adsorbed species $j$, and $C_S$ is the concentration of vacant sites. Step 4 can be used to estimate $C_{N \cdot S}$ by applying the FPE:

$$r_4 = k_4C_{\text{NH} \cdot S}C_S - k_{-4}C_{N \cdot S}C_H = k_4[C_{\text{NH} \cdot S}C_S - C_{N \cdot S}C_H / K_4]$$  \hfill (2)
where \( K_4 = k_4/k_{-4} \). The FPE claims \( r_4/k_4 \approx 0 \), which implies:

\[
C_{N,S} \approx C_{NH,S}C_SK_4/C_{H,S}
\]

Similarly, steps 3, 2, 1, and 6 are used in succession to derive \( C_{NH,S}, C_{NH2,S}, C_{NH3,S} \), and \( C_{H,S} \), respectively. Substitution as needed produces a preliminary rate expression:

\[
-r'^{C}_{NH3} = k_5K^2C^2_N/C^2_S/PH_3
\]

The \( C_S \) derives from the “site balance”: \( C_T = C_S + C_{NH,S} + C_{NH2,S} + C_{NH3} + C_{NS} + C_{H,S} \). Bell and Torrente-Murciano [15] suggest that adsorbed \( N \) atoms are the dominant species. Therefore, the site balance simplifies to: \( C_T \approx C_S + C_{N,S}\), from which:

\[
C_S \approx C_T/(1 + p_{NH3}K/p_{H2}^{1.5})
\]

Substituting Equation (5) into (4) reveals the overall rate expression, assuming desorption and recombination of \( N \) atoms (Step 5) is rate-determining:

\[
-r'^{C}_{NH3} = kp^2_{NH3}/(p_{H2}^{1.5} + \hat{K}p_{NH3})^2
\]

where \( k \) and \( \hat{K} \) are lumped constants: \( k \equiv k_5K^2C^2_N \) and \( \hat{K} \equiv K_1K_2K_3K_4K_6^3 \). For the remaining discussion below, the parameter \( \hat{K} \) replaces \( \hat{K} \).

4.2. Preparation for Calibration of Overall Rate Expression

The CSTR calculation offers a simple way to generate rate data. The ideal CSTR model assumes perfect mixing, with the rate obtained from the steady CSTR species balance. For the \( NH_3 \) decomposition:

\[
r'^{C}_{NH3} = F_{NH3,\theta}X_{NH3}/A_{CSTR}
\]

In this study, the species net rates are related by the stoichiometry: \( NH_3 \to 0.5N_2 + 1.5H_2 \).

\[
-r'^{C}_{NH3} = r'_{N_2}/0.5 = r'_{H_2}/1.5
\]

Using a familiar nomenclature (Fogler, 2020), the species partial pressures are given by:

\[
P_j = P_{NH3,\theta}(\theta_j + \nu_jX_{NH3})/(1 + \epsilon X_{NH3})
\]

where \( \theta_j = F_j/\theta_{NH3,\theta} \) and \( \epsilon = y_{NH3,\theta} \). For the above overall stoichiometry, \( \epsilon = 1 \). The stoichiometric coefficients are: \( \nu_{NH3} = -1, \nu_{N_2} = 0.5, \nu_{H_2} = 1.5 \).

The lumped parameters in the simplified rate expression (Equation (6)) will be calibrated using rate data obtained from Detchem® CSTR simulations run with the detailed \( NH_3 \) decomposition mechanism [8] shown above. Available online [13] with numerous applications, the Detchem® software package is widely used [16,17] and quite versatile. This package executes detailed material, energy, and momentum balances using a user-supplied elementary reaction mechanism and required reactor input and parameter information.

Since the detailed mechanism is validated on experimental data [8], using the simulated rate data here obtained with this mechanism is equivalent to calibrating against experimental data directly. Because the Zhu et al. [8] detailed mechanism does such an excellent job modeling the \( X_{NH3} \) vs. temperature data of Okura et al. [8], calculations with it can be used as the “data” source against which the overall rate expression (Equation (6)) is calibrated. The same catalyst, temperature, and pressure range as Okura et al. [8] are used.

In this study, separate packed bed (plug flow) and continuous stirred tank (perfectly mixed) reactor simulations were performed with Detchem® PBED® and CSTR® applications, respectively. The governing PBED® and CSTR® equations are described in the Detchem® manual [13] and listed elsewhere [18].
At a given temperature and pressure, the Detchem® CSTR® application is run over a wide range of pure NH₃ feed rates $F_{NH3,o}$ to generate gaseous reactor effluent mole fractions, $y_j$. Any pressure drop across the reactor is assumed to be small enough to ignore. The exit mole fractions are used to calculate the corresponding partial pressures, $P_j$. Knowing $P_j$, Equation (9) is used to determine the corresponding NH₃ conversion, $X_{NH3}$:

$$P_{NH3} = P_{NH3,o}(1 - X_{NH3}) / (1 + X_{NH3})$$

(10)

Similarly, $P_{H2}$ and $P_{N2}$ are used to test for $X_{NH3}$ consistency:

$$P_{H2} = P_{NH3,o}(1.5X_{NH3}) / (1 + X_{NH3})$$

$$P_{N2} = P_{NH3,o}(0.5X_{NH3}) / (1 + X_{NH3})$$

(11)

With $X_{NH3}$ data in hand, Equation (7) is used to generate rate $r_{NH3}$ data. At the given temperature, the partial pressure, conversion, and rate ($P_j$, $X_{NH3}$, $r_{NH3}$) data sets, based on exit mole fraction data from the Detchem® CSTR® runs and Equations (7), (10), and (11), are used below to calibrate the overall rate expression (Equation (6)) through the lumped constants $k$ and $\hat{k}$.

**5. Calibration of the Simplified Overall Rate Expression**

An extensive series of Detchem® CSTR® simulations with a pure NH₃ feed over a wide temperature range was performed. Details appear in Table 1. The runs were isothermal at constant pressure. The feed rate range for each temperature was chosen such that the $X_{NH3}$ ranged from near zero to almost 1. The gas volume and catalytic surface area values listed are consistent with the PBED® simulations described later.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Lowest</th>
<th>Highest</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>$1 \times 10^{-11}$</td>
<td>$1 \times 10^{-7}$</td>
</tr>
<tr>
<td>725</td>
<td>$1 \times 10^{-10}$</td>
<td>$1 \times 10^{-5}$</td>
</tr>
<tr>
<td>800</td>
<td>$1 \times 10^{-8}$</td>
<td>$1 \times 10^{-4}$</td>
</tr>
<tr>
<td>875</td>
<td>$1 \times 10^{-7}$</td>
<td>$1 \times 10^{-3}$</td>
</tr>
<tr>
<td>950</td>
<td>$1 \times 10^{-6}$</td>
<td>$1 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Feed Rate (mol/s)</th>
<th>Temperature (K)</th>
<th>Lowest</th>
<th>Highest</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure: $1 \times 10^5$ Pa (constant); Catalyst area: 1.92 $\times 10^{-2}$ m²; Reactor gas volume: 3.33 $\times 10^{-8}$ m³; Feed: pure NH₃, or 25 mol% H₂ or N₂ (balance NH₃) at same total molar rate for selected cases.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For a given temperature and pure NH₃ feed, all $(P_j$, $X_{NH3}$, $r_{NH3}$) data sets were used to calibrate the Equation (6) overall rate expression through the constants $k$ and $\hat{k}$. It should be noted that the Langmuir–Hinshelwood algorithm was used to derive different overall rate expressions, such as Equation (6), each based on a different assumed slow step. All expressions were subjected to testing with the generated $(P_j$, $X_{NH3}$, $r_{NH3}$) data sets. These results are not shown here because the only statistically acceptable rate form was Equation (6), which is based on an assumed slow step of N adatom recombination, which is consistent with Bell and Torrente-Murciano [15].

**Calibration Results**

The generated $(P_j$, $X_{NH3}$, $r_{NH3}$) data sets show that, for all relevant temperatures, the rates decrease with increasing NH₃ conversion. Sample results are shown in Figure 2 (650 K) and Figure 3 (950 K). The simple overall rate expression (Equation (6)) does an excellent job for all pure NH₃ feed cases. It is satisfying that the overall rate expression shows the inflections in the curves at higher $X_{NH3s}$. 
Figure 2. Calculated (Detchem®, Equation (6) overall rate expression with 2 parameters) NH₃ decomposition rates at 650 K for both pure NH₃ and mixed (25 mole% H₂ or N₂, bal. NH₃) feeds (see Table 1). NH₃ conversion varies as a function of total feed rate.

Figure 3. Calculated (Detchem®, Equation (6) overall rate expression with 2 parameters) NH₃ decomposition rates at 950 K for both pure NH₃ and mixed (25 mole% H₂ or N₂, bal. NH₃) feeds (see Table 1). NH₃ conversion varies as a function of total feed rate.
With excellent modeling obtained at all five temperatures for the pure NH$_3$ feed, the rate parameters $k$ and $\hat{k}$ as functions of temperature are presented in Figure 4. The non-Arrhenius curves are each regressed to the form:

$$\ln(k \text{ or } \hat{k}) = a + b(1/T) + c(1/T)^2$$

(12)

![Figure 4](image-url)

Figure 4. Temperature dependencies (point values and regressions) of the two parameters of overall kinetic rate expression (Equation (6)). Units: $k$ (mol-Pa/s-m$^2$); $\hat{k} = \hat{k}\left(Pa^{0.5}\right)$.

The values of $a$, $b$, and $c$ are presented in Table 2. This form is for the sake of convenience. The modest non-linearities in Figure 4 do not necessarily mean a change in rate-determining step over the temperature range. Both parameters $k$ and $\hat{k}$ are lumped, consisting of multiple single constants, each with its own temperature dependence. For example, $\hat{k}$ reflects both dissociative adsorptions and an associative desorption, which would have contrary temperature dependencies.

Table 2. Rate constants for 2-parameter kinetic rate expression (Equation (6)). Form: $\ln(k \text{ or } \hat{k}) = a + b(1/T) + c(1/T)^2$ where $T$ (K).

<table>
<thead>
<tr>
<th></th>
<th>For $k$ (mol-Pa/s-m$^2$)</th>
<th>For $\hat{k}$ (Pa$^{0.5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>$-5.996$</td>
<td>$-6.181$</td>
</tr>
<tr>
<td>$b$</td>
<td>$4.344 \times 10^4$</td>
<td>$2.849 \times 10^4$</td>
</tr>
<tr>
<td>$c$</td>
<td>$-2.610 \times 10^7$</td>
<td>$-1.287 \times 10^7$</td>
</tr>
</tbody>
</table>

Figures 2 and 3 present additional curves, based on the calibrated Equation (6), and data points, based on Detchem$^\circledR$ CSTR$^\circledR$ simulations, wherein 25% of the NH$_3$ feed is replaced with H$_2$ or N$_2$ at the same total feed rate. The H$_2$ cases result in lower NH$_3$ decomposition rates, as suggested by Equation (6). The impact is more pronounced at lower temperatures. The impact of adding N$_2$ in this role is less clear. Equation (6) suggests little impact beyond a dilution effect on H$_2$ and NH$_3$ partial pressures. In both of these tests, the overall simplified rate expression (Equation (6)) calibrated on pure NH$_3$ feed runs did well in predicting the detailed mechanism-based rate results.
6. PBR Species and Energy Balances Used with Overall Rate Expression

The overall calibrated rate expression is now used to simulate NH$_3$ decomposition in the packed bed reactor found in an idealized ammonia fuel cell. The species balances used are shown in Equations (13) and (14). The PBR assumes perfect plug flow.

\[
dF_{\text{NH}_3}/dz = r'_{\text{NH}_3}a_v A_c \quad dF_{\text{N}_2}/dz = r'_{\text{N}_2}a_v A_c
\]

\[
dF_{\text{H}_2}/dz = r'_{\text{H}_2}a_v A_c - k_c P_{\text{H}_2}
\]

Zhu et al. [9] show that the NH$_3$ decomposition can occur within the anode structure of the fuel cell or in the catalytic zone outside the fuel cell itself. If inside, the “diffusion” term on the right side of Equation (14) crudely approximates the passage of H$_2$ through the fuel cell membrane to the cathode, where it is oxidized. If outside, then $k_c = 0$. The PBR energy balance is:

\[
\frac{dT}{dZ} = \frac{\dot{q} + r'_{\text{NH}_3}\Delta H_{r,N\text{H}_3}a_v A_c}{F_{\text{NH}_3}c_p,\text{NH}_3 + F_{\text{N}_2}c_p,\text{N}_2 + F_{\text{H}_2}c_p,\text{H}_2}
\]

If the PBR is assumed adiabatic, then $\dot{q} = 0$. If heat from the cathodic oxidation of H$_2$ conducts through the fuel cell membrane to the anode to satisfy some of the NH$_3$ decomposition endothermicity, the heat transfer rate can be crudely approximated by:

\[
\dot{q} = f k_c P_{\text{H}_2}(-\Delta H_{r,\text{H}_2O})
\]

The thermal data ($c_{p,j}$ and $\Delta H_{r,j}$) are presented in the Appendix A. Constant pressure and ideal gas are assumed throughout this study. Equations (17) provide additional values:

\[
X_{\text{NH}_3} = \frac{(F_{\text{NH}_3,0} - F_{\text{NH}_3})}{F_{\text{NH}_3,0}} \quad P_j = \frac{(F_j/F_T)}{P} \quad F_T = \sum_j F_j
\]

6.1. Packed Bed Reactor Simulations

We begin with packed bed calculations performed using the Detchem® PBED® package. Table 3 presents the data for the simulations. Both high and low pure NH$_3$ feed rates were used, together with a range of feed temperatures. These runs produce the data against which the single rate expression engineering model will be tested.

The engineering model (Equations (13)–(17)) uses the overall single rate expression (Equation (11)) together with the temperature-fitted rate constants in Equation (12). The Polymath® ODE package [19] solved the engineering model for the packed bed reactor.

Figures 5 and 6 present the comparative results. Results in Figure 5 for a pure NH$_3$ feed (1 × 10$^{-5}$ mole/s) at 800 K show that the engineering model does an excellent job predicting the detailed mechanism axial profiles for both NH$_3$ content and reactor temperature. Similar excellent results are shown in Figure 6 over a range of feed temperatures at a higher feed rate (1 × 10$^{-4}$ mol/s). The fits of the NH$_3$ mole fractions are excellent, while the temperatures are predicted within 3 K. With the credibility of the engineering model with single overall rate expression now established, this model was applied for varied applications for which Detchem® PBED® is not applicable.

Table 3. Data for Detchem® PBED® and Engineering Model PBR Simulations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed radius:</td>
<td>$5 \times 10^{-3}$ m</td>
</tr>
<tr>
<td>Bed length:</td>
<td>0.1 m</td>
</tr>
<tr>
<td>Catalyst area/bed volume:</td>
<td>$2.19 \times 10^7$ m$^{-1}$</td>
</tr>
<tr>
<td>Total catalyst area:</td>
<td>0.172 m$^2$</td>
</tr>
<tr>
<td>Bed porosity:</td>
<td>0.28</td>
</tr>
<tr>
<td>Particle diameter:</td>
<td>$2 \times 10^{-3}$ m</td>
</tr>
<tr>
<td>Feed: pure NH$_3$</td>
<td></td>
</tr>
<tr>
<td>Total feed rates:</td>
<td>$1 \times 10^{-5}$, $1 \times 10^{-4}$ mole/s</td>
</tr>
<tr>
<td>Feed temperature range:</td>
<td>650-950 K</td>
</tr>
<tr>
<td>Pressure:</td>
<td>$1 \times 10^5$ Pa (constant)</td>
</tr>
<tr>
<td>Diffusion coefficient $k_c$ (Equation (5)):</td>
<td>$5 \times 10^{-7}$ mol/m$^2$-Pa (used for Figures 7–10 only)</td>
</tr>
<tr>
<td>Heat transfer factor $f$ (Equation (7)):</td>
<td>0.12 (used for Figures 7–10 only)</td>
</tr>
</tbody>
</table>

\[
X_{\text{NH}_3} = \frac{(F_{\text{NH}_3,0} - F_{\text{NH}_3})}{F_{\text{NH}_3,0}} \quad P_j = \frac{(F_j/F_T)}{P} \quad F_T = \sum_j F_j
\]
Figure 5. Comparison of engineering model (EM) with overall kinetic rate expression (Equation (6)) vs. Detchem® with detailed mechanism for axial profiles in adiabatic packed bed reactor feeding pure NH₃ at 1 × 10⁻⁵ mol/s and 800 K (see Table 3 for remaining conditions).

Figure 6. Comparison of engineering model (EM) with overall kinetic rate expression (Equations (6) and (12)) vs. Detchem® with detailed mechanism for adiabatic PBR feeding pure NH₃ at 1 × 10⁻⁴ mol/s (see Table 3 for remaining conditions).
6.2. Extended PBR Simulations

The simulations for Figures 5 and 6 assume the NH₃ decomposition occurs in an adiabatic packed bed reactor external to any fuel cell. However, this decomposition can occur as part of the anode structure of the fuel cell [9]. In this case, H₂ diffusion through the membrane for exothermic oxidation at the cathode accompanies the NH₃ breakdown. In addition, heat transfer from the cathode across the membrane to the anode can supply some of the decomposition endothermicity. Additional PBR calculations were performed to crudely simulate these cases with only the engineering model (Equations (13)–(17)) and simplified rate expression (Equations (6) and (12)). The Polymath® ODE solver [19] was used.

Figures 7–10 show a sequence of additional cases that are easily obtained with the engineering model and overall rate expression, with details provided in Table 3. The three cases shown are H₂ diffusion off (k_e = 0) and adiabatic (f = 0), diffusion on (k_e = 5 × 10⁻⁷ mol/s-m-Pa) and adiabatic, and diffusion on with heat transfer on (f = 0.12). The models of H₂ diffusion and heat transfer are crude, but they illustrate the utility of the engineering model with the overall rate expression.

Figure 7. Impact of H₂ diffusion and heat transfer on axial temperature in PBR; 950 K feed temperature; pure NH₃ feed = 1 × 10⁻⁴ mol/s (see Table 3 for remaining conditions). Calculations based on engineering model with overall decomposition rate expression Equations (6) and (12).

Under adiabatic conditions, the temperature drops rapidly due to the endothermicity of the NH₃ pyrolysis, as shown in Figure 7. This is accompanied by only modest conversion (Figure 8). Loss of H₂ by diffusion has little impact on the bulk flow temperature, even though the drop in H₂ flow rate is large, as shown in Figure 10. Figure 9 shows that the NH₃ flow rate has not dropped much, as is also evident in Figure 8, with only an approximately 23% conversion.

Allowing heat to flow into the packed bed has a significant impact. The slower temperature drop (Figure 7) results in a significantly smaller NH₃ rate (Figure 9) and hence a larger NH₃ conversion (Figure 8). Even more H₂ is available for diffusion (Figure 10). The N₂ flow rate also increases due to the higher NH₃ conversion.
Figure 8. Impact of H₂ diffusion and heat transfer on NH₃ conversion in PBR; 950 K feed temperature; pure NH₃ feed = 1 × 10⁻⁴ mol/s (see Table 3 for remaining conditions). Calculations are based on engineering model with overall decomposition rate expression (Equations (6) and (12)).

Figure 9. Impact of H₂ diffusion and heat transfer on axial NH₃ flow rate in PBR; 950 K feed temperature; pure NH₃ feed = 1 × 10⁻⁴ mol/s (see Table 3 for remaining conditions). Calculations use engineering model with single overall decomposition rate expression (Equations (6) and (12)).
7. Conclusions

An overall rate expression, based on an assumed slow step (desorption of adsorbed N atoms to form N₂) with five remaining elementary steps in fast pseudo-equilibria, has been derived to accurately simulate the decomposition of NH₃ over a Ni-BaZrO₃ catalyst at 1 × 10⁵ Pa at 650–950 K. The expression was calibrated using decomposition rates calculated with a six-step elementary mechanism from the literature proven independently against experimental data. The overall rate expression, with two temperature-dependent parameters, and its implementation in an engineering model successfully predicted NH₃ decomposition performance in a packed bed reactor as calculated with the detailed mechanism. The utility of the engineering model with the overall rate expression was further demonstrated with simulations of NH₃ decomposition in a packed bed reactor allowing for H₂ diffusion and heat transfer in an approximation of a fuel cell anode feeding NH₃. The methodology used in this work is independent of the choice of catalyst. It relies on the availability of a previously published and validated elementary reaction mechanism.

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Nomenclature

- $a$: first of three fitted parameters for lumped kinetic constants (Equation (12))
- $A_c$: packed bed reactor cross section ($m^2$)
- $A_{CSTR}$: catalytic surface area for CSTR ($m^2$)
- $a_P$: catalytic surface area/packed bed volume ($m^2/m^3$)
- $b$: second of three fitted parameters for lumped kinetic constants (Equation (12))
- $c$: last of three fitted parameters for lumped kinetic constants (Equation (12))
- $C_{j:S}$: surface concentration of adsorbed species $j$ (mol/m$^2$)
- $c_{p,j}$: heat capacity of species $j$ ($J/mol-K$)
- $C_S$: concentration of vacant surface sites (mole/m$^2$)
- $C_T$: total concentration of surface sites (mole/m$^2$)
- $f$: assumed fraction of $H_2$ oxidation heat transferring from cathode to anode
- $F_{j}, F_{j:o}, F_T$: molar rate of species $j$ (mol/s) - subscript “o” for feed, “T” for total
- $k$: lumped constant (mol-Pa/s-m$^2$)
- $\hat{k}, \hat{K}$: lumped constants (Pa$^{0.5}$)
- $k_{i,-i}$: rate constants (forward/reverse) for reaction “i” in decomposition mechanism
- $K_i$: equilibrium constant for reaction “i” in decomposition mechanism
- $k_c$: mass transfer coefficient for $H_2$ diffusion across cell membrane (mol/s-m-Pa)
- $P_j$: partial pressure of species $j$ (Pa) - subscript “o” indicates feed
- $q$: local external heat transfer rate in packed bed reactor (J/s-m)
- $r_j^c$: catalytic surface-based reaction rate of species $j$ (mol/s-m$^2$)
- $T$: temperature (K) - subscript “o” indicates feed
- $X_{NH3}$: fractional conversion of NH$_3$
- $y_j$: gaseous species $j$ mole fraction
- $z$: packed bed reactor axial length (m)
- $\delta$: net change in moles per mole of key reactant (NH$_3$) as per reaction stoichiometry
- $\Delta H_{r,j}$: heat of reaction (J/mol of $j$)
- $\epsilon$: product of feed mole fraction of key reactant and net change in moles by reaction
- $\theta_j$: ratio of feed flow rate of species $j$ to feed rate of key reactant (NH$_3$)
- $\nu_j$: stoichiometric coefficient (+/-) assuming key reactant coefficient (NH$_3$) is unity

Appendix A

Table A1. Thermal Data.

<table>
<thead>
<tr>
<th>Species</th>
<th>$c_{p,j}$ (J/mol-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>29.66</td>
</tr>
<tr>
<td>$N_2$</td>
<td>31.42</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>0.02815$T$ + 28.64</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H_{r,j}$ (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$ = 0.5N$_2$ + 1.5H$_2$</td>
<td>45,900. (per mol NH$_3$) at 298 K *</td>
</tr>
<tr>
<td>H$_2$ + 0.5O$_2$ = H$_2$O</td>
<td>$-241,830$. (per mol H$_2$O)</td>
</tr>
</tbody>
</table>

* $\Delta H_{r,T} = \Delta H_{r,298} + (1.5c_{p,H2} + 0.5c_{p,N2} - c_{p,NH3})(T - 298)$.

References

2. Cha, J.; Jo, Y.S.; Jeong, H.; Han, J.; Nam, S.W.; Song, K.H.; Yoon, C.W. Ammonia as an efficient COx-free hydrogen carrier: Fundamentals and feasibility analyses for fuel cell applications. *Appl. Energy* 2018, 224, 194–204. [CrossRef]


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