KINETIC MODELS OF SALT-AMMONIA CHEMISORPTION:
AN OVERVIEW AND COMPARISON

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ABSTRACT

The salt-ammonia chemisorption cycle has been extensively developed in many areas like low-grade heat driven refrigeration, heat pump, thermal storage and power generation. The kinetic models of salt-ammonia chemisorption were reviewed and discussed in this work, and the values of kinetic parameters in different models were summarized and listed for ammonia chemisorption on BaCl₂, CaCl₂, MgCl₂, MnCl₂, NiCl₂, PbCl₂ and SrCl₂. Different methods of modelling kinetics and determining parameters were discussed and compared. It is difficult to conclude which model and parameter values are more accurate than others due to the lack of detailed experimental results and different testing focus and purposes, however, the present paper has given

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some recommendations on how to use these models and the way to determine the necessary parameter values.

**Keywords:** kinetic model, salt ammonia, chemisorption, parameter value, model comparison

**NOMENCLATURE**

- $a$: local volume exchange coefficient (W/K)
- $Ar$: local volume exchange coefficient (s$^{-1}$)
- $C$: constant in Veselovskaya and Tokarev’s model (K$^{-1}$s$^{-1}$)
- $D$: gas diffusivity (m$^2$/s)
- $E$: activation energy (J/mol)
- $E_0$: activation energy in Tykodi’s model (K)
- $G$: resistant coefficient in Zhong et al.'s model (Pa s)
- $\Delta H$: reaction enthalpy change (J/mol NH$_3$)
- $k$: kinetic coefficient (s$^{-1}$) (mol/(s m$^2$)) (K$^{-1}$s$^{-1}$)
- $M$: characteristic coefficient of the pore (-)
- $M_g$: molar mass of gas (kg/mol)
- $m, n$: kinetic coefficient (-)
- $N_g$: molar number of reactive gas per grain (mol)
- $N_s$: molar number of the salt (mol)
- $n_s$: molar number of the salt per volume (mol/m$^3$)
- $P$: pressure (Pa)
- $R$: gas constant (J/(mol K))
- $r$: radius (m)
- $r_g$: grain radius (m)
- $r_c$: unreacted core radius (m)
- $S_{sw}$: heat transfer area (m$^2$)
- $\Delta S$: reaction entropy change (J/(mol K) NH$_3$)
- $s$: coefficient in Arrhenius equation (s$^{-1}$) (mol/(s m$^2$))
- $T$: temperature (K)
- $t$: time (s)
Introduction

The ammonia chemisorption technology has been extensively developed for the application of heat pump and thermal energy storage systems [1]. This technology is favoured for its capability of utilizing low-grade heat source, wide variety of adsorbents with wide range operating temperature and environment-friendly working fluid. The typical ammonia chemisorption system consists of a fixed-bed solid-gas reactor.
and a condenser/evaporator, no mechanical moving component is required. The reversible chemisorption between a metal salt and ammonia is generally formulated as Eq. (1) and is characterized by mono-variant equilibrium according to the Gibbs phase rule:

\[
S.\alpha\text{NH}_3 + \gamma\text{NH}_3 \Leftrightarrow S.\ (\alpha + \gamma)\text{NH}_3 + \gamma\Delta H
\]

where \(S\) is the reactive solid salt, typically alkaline earth or transition metal halogenides, \(\gamma\) is the stoichiometric coefficient, \(\Delta H\) is the reaction heat per mole of ammonia. This reaction is driven by the pressure or temperature equilibrium drop that is defined as the difference between the constraining condition and the equilibrium state. Ammonia is transferred in gaseous phase between reactor and condenser, or between evaporator and reactor.

The ammonia chemisorption is a fairly unstable process. The reaction is violent at the beginning when the state of reactants is distant away from equilibrium. The reaction rate slows down as its state is approaching the equilibrium and eventually reaches equilibrium. The kinetics is very important knowledge for system dimensioning, optimal design and controlling, however, compared to the research on other subjects of chemisorption technology, there is relatively scarce information on chemisorption kinetics. Different kinetic models have been proposed by different authors as they have studied different reactive mediums contained in different reactors that have different geometric structure in different scales, meanwhile have adopted different hypotheses to simplify their modelling to more or less extent for their specific purpose and focus.

The transient nature of chemisorption is related to the kinetics of the solid-gas reaction and the properties of the reactor/reactant regarding heat and mass transfer, which can have impact on the determination of kinetic parameters in the numerical resolution of a set of differential equations. This makes it difficult for all different researchers who use different methods to reach on one single universal kinetic expression that works satisfactorily for each case, unless an agreement can be reached to standardize the kinetic test apparatus, experimental conditions and material related specifications. However, it is very unlike to realize...
realize that because different researchers resorted to different methods according to their specific problems (different system designs, different applications, different available heat sources or heat sinks, etc.). For example, the semi-empirical local/global models that have been used in most cases to make relatively rapid calculation for system dimensioning can be only valid in situations of geometric similarity for the purposes of scale changes under the exact or at least a similar set of conditions [2, 3]. Therefore different models and different values of parameters even for the same model have been reported by different authors.

The current paper chapter firstly summarized different methods of kinetic determination, and then reviewed the kinetic models of the chemisorption between ammonia and metal halide salts, including BaCl₂, CaCl₂, MgCl₂, MnCl₂, NiCl₂, PbCl₂ and SrCl₂, and presented the corresponding values of kinetic parameters. By comparing the calculation results of conversion evolution based on those models, the difference between them has been discussed and some recommendations were also given for further investigation and model application.

2. KINETIC MODELS

Figure 1 shows the synthesis and decomposition of ammonia-metallic salt chemisorption in the P-T diagram and the schematic of a typical chemisorption system. The ammonia liquid/vapour equilibrium line and the chemisorption equilibrium line are plotted according to the Van't Hoff equation (Eq. (2)), which has linear relationship between ln(Peq) (bar) and −1000/T (K).

\[
\ln(P_{eq}) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}
\]

(2)

where \(\Delta H\) and \(\Delta S\) are the reaction enthalpy and entropy respectively, \(R\) is the gas constant. Touzain et al. [4] have calculated the values of \(\Delta H\) and \(\Delta S\) of the coordination reaction between ammonia and approximately 350
different metallic salts, based on the experimental results selected from about 70 references, some of which could track back to about 1900. Neveu and Castaing [5] compiled the data of 36 most commonly used metallic ammines from more recent experimental works.

As shown in Figure 1, a reactor and a condenser/evaporator can form a basic single stage ammonia chemisorption system. Compared to the solid-gas reaction rate, the liquid-vapour phase change in the condenser/evaporator is instantaneous; moreover, to design the test rig for kinetic parameter determination, usually the condenser/evaporator is greatly oversized relative to the capacity of the reactor to minimise the thermal effects on the solid-gas reaction rate due to evaporation and condensation process [2, 3]. Therefore, the condenser/evaporator dominates the pressure inside the reactor, and this pressure i.e., the constraining pressure, $P_c$, is corresponding to the liquid-vapour equilibrium at the temperature of the heat source/sink at the condenser/evaporator ($T_{eva/con}$). The equilibrium temperature of the chemisorption, $T_{eq}$, can be reversely derived from the calculation of Eq. (2) by using $P_c$, as illustrated in Figure 1. Meanwhile the constraint temperature of the chemisorption reaction, $T_c$, can be the temperature of heat transfer fluid (HTF) which is heating/cooling the reactor; or, for the local reactant, the constraint temperature is usually considered as the local reactant temperature, which is dominated by the heat transfer between HTF and reactant and also the heat conduction within the reactant.

For synthesis, the constraint temperature $T_{c,s}$ should be lower than the equilibrium temperature ($T_{c,s} < T_{eq}$) so that the corresponding equilibrium pressure can be lower than the constraint pressure ($P_{eq,s} < P_c$); on the contrary for decomposition, the thermal condition required should be $T_{c,d} > T_{eq}$ and $P_{eq,d} > P_c$. The difference between the state of the reactant and its corresponding equilibrium state is known as the equilibrium drop [2, 3, 5], can be expressed as the pressure drop $|P_c - P_{eq}|$ or the temperature drop $|T_c - T_{eq}|$. The equilibrium drop has dominative impact on the reaction rate, the larger equilibrium drop drives the faster reaction and consequently increases the system thermal power.
Figure 1. $P-T$ diagram and schematic system of ammonia chemisorption.

2.1. Model Development Methods

The generalized expression of the reaction rate, $dx/dt$, is given as Eq. (3) [2]:

$$dx/dt = \frac{1}{2} \left( \frac{p_{sa}}{p_s} - 1 \right)$$
\[
\frac{dx}{dt} = k(P,T)f(x)
\]

where \(x\) is the degree of conversion of the reaction; the term of \(k(P,T)\) is known as specific rate representing the influence of the deviation of operating conditions from equilibrium conditions on the reaction rate; the function \(f(x)\) reflects the variations of the reactivity with the progression of the reaction and the changes in physical structure of the reactive medium [1, 3]. Experimental results has evidenced that the chemisorption reaction rate is clearly dependent on conversion \(x\), pressure \(P\) and temperature \(T\). In present paper, the degree of conversion \(x\) is defined as 0 to 1 during the synthesis and as 1 to 0 during the decomposition, viz. the reaction rate \(dx/dt\) is positive when synthesis and negative when decomposition.

Numerous forms of \(k(P,T)\) have been proposed. Depending on the hypotheses adopted by different authors in the construction of their models and levels of knowledge involved, Table 1 summarizes different methods of modelling and parameter determination. For most studies so far, imperfect knowledge of the reactive medium and the process that governs local transformations that is required to develop a phenomenological model has led to the choice of an analogical model, which is developed from phenomenological model but has simpler expression without precise physical interpretation for different terms or for parameter identification. Analogical model should contain fewer numbers of parameters than a phenomenological model.

The analogical models studied so far can be further divided into three categories, local, global and analytical ones, depending on the methods used to determine the kinetic parameters [6, 7]. In the similar principle, the phenomenological model can be classified as a local model that is detailed at the grain level, in comparison, the analogical local models is ‘local’ at the relatively larger scale, e.g., on a small element of volume at a macroscopic level. Figure 2(a) shows the determination procedures of phenomenological kinetic model at grain level based on the measured microscopic properties, analogical local and global kinetic models based on experimental results of small lab-scale prototypes.
<table>
<thead>
<tr>
<th>Model type</th>
<th>Hypothesis</th>
<th>Application</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenomenological model</td>
<td>In the grain:</td>
<td>• Detailed design, dimensioning and fine optimization of the reactive reactor (in various reactor geometries) and the thermochemical machines under various working conditions</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Each grain is considered spherical and to keep this spherical form throughout the reaction.</td>
<td>• Study on the limiting phenomena</td>
<td>[20-26]</td>
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<tr>
<td></td>
<td>• The porosity and the numbers of the pores remain constant.</td>
<td></td>
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<tr>
<td></td>
<td>• The structure change is only expansion and shrinking in synthesis and decomposition reaction respectively.</td>
<td></td>
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<td></td>
<td>• Uniform temperature</td>
<td></td>
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<tr>
<td></td>
<td>• An interface separates solid products and reactants. During the reaction, the interface moves towards the centre of the grain, keeping its initial form.</td>
<td></td>
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<tr>
<td></td>
<td>• No gas products.</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>• Gas diffusion in the radial direction is much faster than the movement of the interface.</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>• Knowledge model, detailed analysis of the reactive medium in particulate level (e.g., grain particle)</td>
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<tr>
<td></td>
<td>• Requires profound understanding of precision phenomena and physicochemical properties (e.g., grain size, geometric structure of the grain changing with the reaction progress);</td>
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<td></td>
<td>• For the cases of using composite adsorbent that is formed by consolidating the reactive medium with a porous supporting matrix, the granulometric repartition, porosity and inter- and intra-granular diffusivity must all be known.</td>
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<tr>
<td></td>
<td>• The function ( f(x) ) represents the evolution of the reacting interface</td>
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</tr>
<tr>
<td>Model type</td>
<td>Hypothesis</td>
<td>Application</td>
<td>Ref.</td>
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</tbody>
</table>
| Analogical model    | • Not knowledge model, attempts to reproduce their overall effect without detailed analysis of the elementary mechanisms of the reaction  
                      ● The reactive medium is considered as an equivalent entity at a macroscopic level;  
                      ● Thermochemical considerations on analogies with simple physicochemical processes and on classical (non-catalytic) heterogeneous kinetics or homogeneous reactions | In a small element of volume:  
                      ● Consider local and uniform variables ($T$ and $P$) and rely on local laws of energy and/or mass conservation.  
                      ● With $P(t, r)$ and $T(t, r)$ known experimentally in a medium, the kinetic equation $\frac{dx}{dt} = f(x, T, P)$ can be resolved for $x$, independently of heat and mass transfer models. The kinetic coefficient can be identified by comparing these results with the measured global advancements. | [6, 12, 13, 19, 28, 30, 34] |
| Local method        | • Require the local phenomena to determine the specific profile of the temperature, pressure and the reaction rate within the reactive medium.  
                      ● Coupling heat transfer, and/or mass transfer with a kinetic law of the chemical reaction to determine kinetic parameters  
                      ● A numerical resolution of a set of governing equations discretized in space and time | • Optimization and scale changes of the reactor (or adsorber) in geometric similarity and determination of the optima reactivity in order to meet the technical and/or economic requirements (mass, volume, cost, performance). For example, in the typical cylindrical reactive beds, a local model can be used to optimize the thickness in radial direction of the reactive medium in relation to the two opposing variables which are the available energy and the thermal power.  
                      ● Only valid under the exact conditions used to determine the parameters, or under a similar set of conditions. |
<table>
<thead>
<tr>
<th>Model type</th>
<th>Hypothesis</th>
<th>Application</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global method</td>
<td>In the whole volume:</td>
<td>• With the same purpose and the scope of model application as the local models, it is aimed to simplify the work of preliminary plan and unit optimal control in comparison with the local models</td>
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<td></td>
<td>• Uniform variables ((T \text{ and } P)) throughout the reactive medium (e.g., in the cases of using the composite of reactive salts impregnated in the graphite matrix that has high conductivity to enhance heat transfer and foliate structure to ensure rapid gas diffusion), and consider the average local values of the degree of conversion in the whole volume whereby the global extent attains the desired value</td>
<td>• Especially suitable to be used as a basis for the preliminary pre-dimensioning of the larger scale installation.</td>
<td>[3, 10, 18, 27-29, 33, 35-38]</td>
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<td></td>
<td>• Minimize any limitation on the progression of the reaction due to heat transfer and mass transfer.</td>
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<td></td>
<td>• Determine the kinetic parameters without the coupling with heat/mass transfer.</td>
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<td></td>
<td>• Describe the couplings between the reactor and the peripheral components of a complete system (evaporator/condenser, heat sinks and sources, etc.)</td>
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<td></td>
<td>• A numerical resolution of a set of differential equation only  (\text{discretized} ) in time</td>
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<td></td>
<td>• Involve an empirical element, known as semi-empirical models; cannot be calculated directly and must be established by calibrating the model against experimental values</td>
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<tr>
<td>Model type</td>
<td>Analytical method</td>
<td>Hypothesis</td>
<td>Application</td>
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<td></td>
<td>• The local extent profile in the reaction front can be approximated by a linear function of the local dimensionless temperature</td>
<td>• No limitation by mass transfer in the reactive medium, and consider the average local values during the reaction time whereby the global extent attains the desired value</td>
<td>• Considerably simplify the dimensioning procedure in comparison with dynamic models, to enable quick roughing out and optimization in the pre-dimensional of thermochemical machines</td>
</tr>
<tr>
<td></td>
<td>• A single differential equation (heat transfer equation) only related to the space variable</td>
<td></td>
<td>• With the given heat source or heat sink and thermal characteristics of the reactive medium in order to obtain an average thermal power over a certain reaction duration: 1. calculate the constraint temperature for a given reactor; 2. determine the geometry of a reactor under an imposed constraint temperature.</td>
</tr>
</tbody>
</table>
Kinetic Models of Salt-Ammonia Chemisorption

(a) Determination of phenomenological kinetic model (grain level), analogical local and global kinetic models (small lab-prototype level)

(b) Dimensioning using phenomenological kinetic model, analogical local or global kinetic models

(c) Dimensioning using analytical model

Figure 2. Comparison of procedures of different modelling methods.
For the analogical local and global models, the relatively precise definition of the geometry of the model element is required and the models developed and calibrated based on the measured results on this reference volume are only suitable for those in the similar geometry. However, such precise geometric definition actually is not easily defined during the pre-sizing phase of a unit. Without the precise knowledge of geometric structure as well as the constraints that are imposed on the reactor, parameters are initially fixed in an arbitrary way for a dynamic simulation that uses either local or global models for reactor dimensioning. One proceeds the dynamic calculation to obtain the variables of thermal power and global reaction conversion. Usually, in order to achieve the desired performance, it has to carry out several rounds of dynamic calculation by successive iterations of various parameters in order to reach the average thermal power desired over a given time step, as shown in Figure 2(b). Apparently such dynamic simulation is sometimes a bit complex and leads to lengthy calculation. Because in most cases, the dimensioning of industrial machines follows a quasi-stationary working mode, the transient regimes have little influence on the dimensioning, the dimensioning procedure was proposed to be simplified to a resolution of one single differential equation (heat transfer equation), which is analytic and links together various parameters of different components that influence the reactor performance, thus allowing a rapid dimensioning of the reactor [6, 7] as shown in Figure 2(c).

2.2. Various Expression of Kinetic Models

2.2.1. Tykodi’s Model (1979)

Spinner and Rheault [8] conducted a detailed comparison on different forms of specific rate, $k(P, T)$, and recommended the following models based on Tykodi’s model [9] for ammonia synthesis and decomposition respectively as it includes a term for the deviation from equilibrium conditions in logarithmic form, as given in the following equations:
\[ \frac{dx}{dt} = k_s (1 - x) \exp \left( \frac{-F_0}{T} \right) \ln \frac{P_c}{P_{eq}(T)} \]  

\[ \frac{dx}{dt} = k_d x \exp \left( \frac{-F_0}{T} \right) \ln \frac{P_c}{P_{eq}(T)} \]  

The Boltzmann’s factor, \( \exp \left( \frac{-F_0}{T} \right) \), is used to describe the temperature dependence of chemical reaction rate.

Tykodi’s model has been further developed by Lebrun and Spinner [3] to be adapted to three cases with the hypotheses of three different kinetic-limiting factors: the factor of mass transfer rate through a layer of adsorbed gas, the chemical reaction, and the mass transfer through the product of the reaction. Since these is only one kind of gas involved in the solid-gas chemisorption reviewed here, i.e., ammonia, only the latter two hypotheses are relevant for modelling and presented in kinetic equations in Eq. (5) and (6), respectively.

\[ k(P, T) = k_1 \cdot \exp \left( \frac{-F_1}{T} \right) \cdot \ln \left( \frac{P_1}{P_{eq}(T)} \right) \]  

\[ k(P, T) = k_2 \cdot \exp \left( \frac{-F_2}{T} \right) \cdot \ln \left( \frac{P'}{P_i} \right) \]  

where \( P_i \) is the pressure at the reacting interface and \( P' \) is the pressure at the surface of the salt. The authors built a global model of solid-gas reaction between calcium chloride and methylamine with the hypothesis of chemical reaction as the limiting factor, while assuming the leafy structure of the expanded graphite mixed with the reactive salt ensured the efficient gas diffusion. The values of kinetic parameters were determined on the basis of lab scale experiments using 50 g calcium chloride.

Neveu and Castaing-Lasvignottes [10] obtained the values of kinetic parameters for \( \text{MnCl}_2-\text{NH}_3 \) and \( \text{NiCl}_2-\text{NH}_3 \) reactions, as listed in Table 2, by fitting Tykodi’s equations with experimental results reported in the work [11].
Table 2. Values of parameters in Tykodi’s model for MnCl$_2$-NH$_3$ and NiCl$_2$-NH$_3$ chemisorption

<table>
<thead>
<tr>
<th></th>
<th>$k_s$ (s$^{-1}$)</th>
<th>$k_d$ (s$^{-1}$)</th>
<th>$E_0$ (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCl$_2$-6/2$\cdot$NH$_3$</td>
<td>0.92</td>
<td>0.59</td>
<td>1390</td>
<td>Neveu and Castaing-Lasvignottes [10], 1997</td>
</tr>
<tr>
<td>NiCl$_2$-6/2$\cdot$NH$_3$</td>
<td>0.43</td>
<td>0.26</td>
<td>1404</td>
<td></td>
</tr>
</tbody>
</table>

2.2.2. Mazet et al.’s Model (1991)

For the reversible reaction between calcium chloride and methylamine in heterogeneous kinetics, Mazet et al. [2] used the format of $k(P,T)$ as expressed in Eq. (7):

$$k(P,T) = Ar \cdot f'(P,T)$$ \hspace{1cm} (7)

where the Arrhenius term $Ar = xe^{(-E/RT)}$ from Arrhenius law expresses the increase in reaction rate with temperature in homogeneous kinetics. However, this term can be considered to practically equivalent to a constant during the reaction, because the experimental results revealed that the contribution of the Arrhenius term to the reaction rate was fairly low compared to the degree of deviation from the equilibrium state (the term $f'(P, T)$), furthermore, authors suggested that it was impossible to identify the two parameters $s$ and $E$ separately.

Based on the experimental tests under various constraint conditions, the linear function of $f'(P, T) = \frac{P_c - P_{eq}(T)}{P_c}$ rather than the logarithmic form in Tykodi’s model was proposed and analysed. Moreover, compared to Tykodi’s model, a pseudo-order of the reaction, $m$, was introduced to the $f(x)$ term for the calcium chloride/methylamine reaction, and the value of $m$ was believed to be between 0 and 2, but no physical meaning though.

The complete expression of kinetic model for synthesis and decomposition respectively is:

$$\frac{dx}{dt} = Ar_s(1 - x)^m \frac{P_c - P_{eq}(T)}{P_c}$$ \hspace{1cm} (8a)
This model has been widely used for ammonia-based chemisorption with different metal salts, and the parameter values that have been reported and studied are presented in Table 3. It should be noted that only Wang et al. [18] and Mofidi and Udell [19] have conducted experiments so that to fit the kinetic model using experimental results for the determination of various parameter values; whereas, others either cited other researchers’ work or has left out the details of the data source. Wang et al. [18] experimented 0.24-0.32 L salt-expanded graphite composite contained in a cylindrical reactor with a central hole for ammonia flow, which was immersed in a thermostatic bath with controlled conditions; Mofidi and Udell tested 0.35 L salt-expanded graphite composite in a cylindrical reactor that was cooled by air.

Table 3. Values of parameters in Mazet et al.’s model for different ammonia chemisorption

<table>
<thead>
<tr>
<th></th>
<th>$A_r$ (s$^{-1}$)</th>
<th>$m_r$ (%)</th>
<th>$A_d$ (s$^{-1}$)</th>
<th>$m_d$ (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCl$_2$·6/2$\mathrm{NH}_3$</td>
<td>0.0010187</td>
<td>1.185</td>
<td>0.0010187</td>
<td>1.185</td>
<td>Han et al. [12], 2000</td>
</tr>
<tr>
<td>MnCl$_2$·6/2$\mathrm{NH}_3$</td>
<td>0.0033</td>
<td>1.0</td>
<td>0.0033</td>
<td>1.0</td>
<td>Dutour et al. [13], 2005</td>
</tr>
<tr>
<td>MnCl$_2$·6/2$\mathrm{NH}_3$</td>
<td>0.0003</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>Azoumah et al. [14], 2007</td>
</tr>
<tr>
<td>MnCl$_2$·6/2$\mathrm{NH}_3$</td>
<td>0.001019</td>
<td>1.185</td>
<td>0.0028</td>
<td>1.0</td>
<td>Lyakh et al. [15], 2013</td>
</tr>
<tr>
<td>BaCl$_2$·8/0$\mathrm{NH}_3$</td>
<td>0.0033</td>
<td>1.0</td>
<td>0.0033</td>
<td>1.0</td>
<td>Le Pierrès et al. [16], 2007</td>
</tr>
<tr>
<td>BaCl$_2$·8/0$\mathrm{NH}_3$</td>
<td>0.0001</td>
<td>1.0</td>
<td>0.0001</td>
<td>1.0</td>
<td>Le Pierrès et al. [17], 2008</td>
</tr>
<tr>
<td>BaCl$_2$·8/0$\mathrm{NH}_3$</td>
<td>0.0125</td>
<td>2.104</td>
<td>0.0195</td>
<td>1.005</td>
<td>Lyakh et al. [15], 2013</td>
</tr>
<tr>
<td>CaCl$_2$·4/2$\mathrm{NH}_3$</td>
<td>0.0287</td>
<td>1.78</td>
<td>0.0045</td>
<td>0.468</td>
<td>Wang et al. [18], 2010</td>
</tr>
<tr>
<td>CaCl$_2$·8/4$\mathrm{NH}_3$</td>
<td>0.0125</td>
<td>2.104</td>
<td>0.0195</td>
<td>1.005</td>
<td></td>
</tr>
<tr>
<td>MgCl$_2$·6/2$\mathrm{NH}_3$</td>
<td>0.006036</td>
<td>1.185</td>
<td>-</td>
<td>-</td>
<td>Mofidi and Udell [19], 2017</td>
</tr>
</tbody>
</table>
Table 4 Values of parameters in Eq. (9) for MnCl$_2$-NH$_3$ and NiCl$_2$-NH$_3$ chemisorption

<table>
<thead>
<tr>
<th></th>
<th>$A_r_1$ (s$^{-1}$)</th>
<th>$A_r_2$ (s$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCl$_2$-6/2 NH$_3$</td>
<td>0.031</td>
<td>0.027</td>
<td>Neveu and Castaing-Lasvignottes [10], 1997</td>
</tr>
<tr>
<td>NiCl$_2$-6/2 NH$_3$</td>
<td>0.018</td>
<td>0.0095</td>
<td></td>
</tr>
</tbody>
</table>

In the study on dynamic process of solid gas transformer, Neveu and Castaing-Lasvignottes [10] made slight changes of kinetic equations on the basis of Mazet et al.’s model to fit better with the measured data of MnCl$_2$-6/2 NH$_3$ and NiCl$_2$-6/2 NH$_3$ reactions performed by differential microcalorimetry [11, 20]. The pseudo-order of the reaction, $m$, was set to 1 and the term of $f'(P,T)$ was given as $\frac{P_c-P_{eq}(T)}{P_{eq}(T)}$, and the complete equation is expressed in Eq. (9) while the corresponding parameter values determined were presented in Table 4.

$$\frac{dx}{dt} = A_r_2 \left(1 - x\right) \frac{P_c-P_{eq}(T)}{P_{eq}(T)} \quad (9a)$$

$$\frac{dx}{dt} = A_r_3x \frac{P_c-P_{eq}(T)}{P_{eq}(T)} \quad (9b)$$

In Neveu and Castaing-Lasvignottes’s work [10], two global models respectively based on Tykodi’s model and Mazet et al.’s model and the phenomenological model proposed by Goetz and Marty [20] were compared using the same measured data in works [11, 20]. The comparative results showed the two global models gave similar results, and the Tykodi’s model was slightly less adapted; while Goetz and Marty’s phenomenological model presented a great improvement.

2.2.3. Goetz and Marty’s Model (1992) and Lu et al.’s Model (1996)

A grain-level phenomenological kinetic model has been developed and proposed by Goetz and Marty [20]. In this model, the chemisorption is
assumed to occur in a sphere grain and this sphere has uniform temperature throughout the reaction, according to Mazet et al.’s study on a grain about 1.0 mm in diameter the temperature difference between the surface of the grain and the reactional interface is negligible (below 0.1°C). Therefore, for the studied spherical, isothermal grains, the regime was identified as the coupling between mass transfer and chemical reaction. As shown in Figure 3, there exists an interface between the unreacted core and the chemisorption resultant. This interface moves from the edge of the grain towards the centre. With the assumption of constant porosity and constant pore diameter within the grain during the reaction, the radius of the grain increases as it expands during the synthesis and decreases as it contracts during the decomposition. In this work, after obtaining kinetics at the grain level, the global degree of conversion at a pellet level was proposed to be subsequently determined through the resolution of the heat and mass transfer equations with the grain kinetics. The mass transfer was ignored but only heat transfer was coupled with the grain kinetics for the simulation of the reactive bed conversion in Goetz and Marty’s work [20].

The reactive gas diffuses through the resultant layer driven by the force of pressure difference between constraining pressure ($P_c$) and interface pressure ($P_i$), therefore, the mass transfer equation can be obtained as Eq. (10):

$$\frac{dN_g}{dt} = \frac{r_g r_c}{r_g - r_c} \frac{4\pi}{RT} D (P_c - P_i)$$

where $N_g$ is the molar number of reactive gas per grain, $r_g$ is the radius of grain, $r_c$ is the radius of unreacted core, $D$ is the gas diffusivity. $dN_g/dt$ was positive for synthesis and negative for decomposition. The value of $D$ is highly dependent on the flow rate, and according to the microcalorimetric experiments, the gas flow at the grain level in chemisorption was identified as a Knudsen type flow [21, 22] and $D$ can be calculated by Eq. (11):

$$D = \frac{4M\epsilon\bar{u}}{3}$$
where $M$ is the characteristic coefficient of the pore and was suggested between 0.39 and 0.55 [20, 21], $\varepsilon$ is the porosity, $\psi$ is the hydraulic pore radius, $\tilde{u}$ is the quadratic velocity of the gas ($= \frac{\sqrt{8RT}}{\pi M_g}$). Meanwhile, the rate of reactive gas consumption/generation can also be determined by the kinetic of the chemisorption, as given by the following equations for synthesis and decomposition respectively:

$$\frac{dN_g}{dt} = 4\pi r_c^2 k_s \left( \frac{p_i}{P_{eq}(T)} - 1 \right)^{m_s} \quad \text{(12a)}$$

$$\frac{dN_g}{dt} = -4\pi r_c^2 k_d \left( 1 - \frac{p_i}{P_{eq}(T)} \right)^{m_d} \quad \text{(12b)}$$

where $k_s$, $k_d$, $m_s$, and $m_d$ are the kinetic coefficients. The grain expands/contracts in synthesis/decomposition, the radius can be evaluated by the following equation:

$$r_g^3 = r_c^3 + \left( r_g^3 - r_c^3 \right) \frac{v_{md}}{v_{ms}} \quad \text{(13a)}$$

$$r_g^3 = r_c^3 + \left( r_g^3 - r_c^3 \right) \frac{v_{ms}}{v_{md}} \quad \text{(13b)}$$

where $r_{gs}$ and $r_{gd}$ are the initial grain radius before synthesis and decomposition respectively, $v_{ms}$ and $v_{md}$ are the molar volume of the grain (m$^3$/mol) before synthesis and decomposition respectively. Then the reaction conversion of the grain can be determined by Eq. (14a) and (14b) respectively for synthesis and decomposition:

$$x = 1 - \left( \frac{r_c}{r_{gs}} \right)^3 \quad \text{(14a)}$$
\[ x = \left( \frac{r_c}{r_{gd}} \right)^3 \]  \hspace{1cm} (14b)

The interface pressure, \( P_i \), was believed to be between the constraint pressure (\( P_c \)) and the pressure in the case of diffusional limitation, and can be calculated by dichotomy [20]. Alternatively, the value of variables, \( N_g \), \( P_i \), \( r_g \), \( r_c \) and \( x \) can be obtained in the resolution of a set of equations, including Eq. (10-14) and the mass balance equation of the reactive gas as given in Eq. (15) [22, 23]:

\[
\frac{dN_g}{dt} = -4\pi r_c^2 \gamma \frac{1}{v_{ms}} \frac{dr_c}{dt} \]  \hspace{1cm} (15a)

\[
\frac{dN_g}{dt} = 4\pi r_c^2 \gamma \frac{1}{v_{md}} \frac{dr_c}{dt} \]  \hspace{1cm} (15a)
It is noted that by combining Eqs. (12), (14) and (15), one can obtain the expression of the reaction rate, $\frac{dx}{dt}$, that has similar form to Mazet et al.’s model, as giving in the following equations:

$$\frac{dx}{dt} = \frac{3k_s v_{ma}}{\gamma r_{g,s}} (1 - x)^{2/3} \left( \frac{p_i}{P_{eq}(T)} - 1 \right)^{m_s}$$  \hspace{1cm} (16a)

$$\frac{dx}{dt} = \frac{3k_d v_{ma}}{\gamma r_{g,d}} x^{2/3} \left( 1 - \frac{p_i}{P_{eq}(T)} \right)^{m_d}$$  \hspace{1cm} (16a)

The parameters in Goetz and Marty’s model were identified for different ammonia-salt reactions by comparing calculated values with the experimental ones on milligrams of reactive medium, while applying microcalorimetric method to avoid limitation of heat and mass transfer within the pellets. These values were presented in Table 5, based on the measurements on 6 mg salts contained in a cell less than 1 cm in diameter [20, 22, 24].

Table 5. Values of parameters in Goetz and Marty’s model for MnCl$_2$-NH$_3$, BaCl$_2$-NH$_3$, and NiCl$_2$-NH$_3$ chemisorption

<table>
<thead>
<tr>
<th></th>
<th>MnCl$_2$-6/2 NH$_3$ [20, 22]</th>
<th>BaCl$_2$-8/0 NH$_3$ [22, 24]</th>
<th>NiCl$_2$-6/2 NH$_3$ [22, 24]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_s$ (mol/(s m$^2$))</td>
<td>0.17</td>
<td>0.15</td>
<td>0.73</td>
</tr>
<tr>
<td>$m_s$ (-)</td>
<td>0.77</td>
<td>1.64</td>
<td>2.16</td>
</tr>
<tr>
<td>$k_d$ (mol/(s m$^2$))</td>
<td>0.38</td>
<td>0.56</td>
<td>0.44</td>
</tr>
<tr>
<td>$m_d$ (-)</td>
<td>2.2</td>
<td>3.23</td>
<td>2.52</td>
</tr>
<tr>
<td>$r_{g,s} \times 10^4$ (m)</td>
<td>3.9</td>
<td>4.8</td>
<td>4.2</td>
</tr>
<tr>
<td>$r_{g,d} \times 10^4$ (m)</td>
<td>4.9</td>
<td>7.6</td>
<td>5.3</td>
</tr>
<tr>
<td>$M$ (-)</td>
<td>0.47</td>
<td>0.48</td>
<td>0.48</td>
</tr>
<tr>
<td>$\varepsilon$ (-)</td>
<td>0.16</td>
<td>0.1</td>
<td>0.13</td>
</tr>
<tr>
<td>$\psi \times 10^9$ (m)</td>
<td>1.33</td>
<td>1.96</td>
<td>1.51</td>
</tr>
</tbody>
</table>

Lu et al. [21, 25, 26] modified the kinetic part of Goetz and Marty’s model to represent the experimental results with better accuracy, and to make the linearization of the source term during the discretization of the
differential equation easier. The Arrhenius term was introduced to the kinetic equation to correlate the temperature, Eq. (12) then becomes:

\[
\frac{dN_g}{dt} = 4\pi r_c^2 s_g \exp \left( -\frac{E_s}{RT_c} \right) \left( \frac{P_i}{P_{eq(T_c)}} - 1 \right) \tag{17a}
\]

\[
\frac{dN_d}{dt} = 4\pi r_c^2 s_d \exp \left( -\frac{E_d}{RT_c} \right) \left( \frac{P_i}{P_{eq(T_c)}} - 1 \right) \tag{17b}
\]

The corresponding parameters are listed in Table 6.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MnCl(_2)-6/2 NH(_3) ([21])</th>
</tr>
</thead>
<tbody>
<tr>
<td>s(_g) (mol/(s m(^2)))</td>
<td>2.82</td>
</tr>
<tr>
<td>E(_s) (J/mol)</td>
<td>7140</td>
</tr>
<tr>
<td>s(_d) (mol/(s m(^2)))</td>
<td>2.25</td>
</tr>
<tr>
<td>E(_d) (J/mol)</td>
<td>9430</td>
</tr>
<tr>
<td>r(_r) \times 10(^7) (m)</td>
<td>5.48</td>
</tr>
<tr>
<td>(\varepsilon) (%)</td>
<td>0.18</td>
</tr>
<tr>
<td>(\psi) \times 10(^9) (m)</td>
<td>1.31</td>
</tr>
</tbody>
</table>

2.2.4. Iloeje et al.’s Model (1995)

The specific reaction rate in Iloeje et al.’s model \([27]\) is a function of the temperature equilibrium drop rather than the pressure equilibrium drop, as shown in Eq. (18):

\[
\frac{dx}{dt} = k_s (1 - x)(T_{eq(P)} - T_c) \tag{18a}
\]

\[
\frac{dx}{dt} = k_d x(T_{eq(P)} - T_c) \tag{18b}
\]

where, \(k_s\) and \(k_d\) were not constant but correlated with the constraint pressure based on experimental results. The correlation reported for SrCl\(_2\)
ammines was adopted by [27] for the kinetics of CaCl₂ ammines because of the similarities between the ammines of these two salts, as given in Table 7.

Table 7. Values of parameters in Iloje et al.’s model for several ammonia chemisorption

<table>
<thead>
<tr>
<th>Compound</th>
<th>(k_s \cdot k_d (K^{-1} \cdot s^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl₂-4/2 NH₃</td>
<td>((0.4P_c + 1.7) \times 10^5)</td>
<td>Iloje et al. [27], 1995</td>
</tr>
<tr>
<td>CaCl₂-8/4 NH₃</td>
<td>30000(N₂γΔHr), local model</td>
<td>Neveu and Castaing-Lasvignottes [10], 1997</td>
</tr>
<tr>
<td>MnCl₂-6/2 NH₃</td>
<td>(U_{\alpha} S_{\alpha}/(n_{\gamma} \Delta H_{l}))</td>
<td>Neveu and Castaing-Lasvignottes [10], 1997</td>
</tr>
<tr>
<td>NiCl₂-6/2 NH₃</td>
<td>(10000(N_{\gamma}\Delta H_{l}), \text{global model})</td>
<td>Goetz and Llobet [28], 2000</td>
</tr>
<tr>
<td>MnCl₂-6/2 NH₃</td>
<td>(28000(N_{\gamma}\Delta H_{l}))</td>
<td>Lépinasse et al. [29], 2001</td>
</tr>
<tr>
<td>PbCl₂-8/3.25 NH₃</td>
<td>(28000(N_{\gamma}\Delta H_{l}))</td>
<td>Lépinasse et al. [29], 2001</td>
</tr>
</tbody>
</table>

Neveu and Castaing-Lasvignottes [10] proposed a concept of equivalent temperature that was suggested to be a complemented to the kinetic law. It was stated that a reliable model with respect to both dynamic evolution (power criterion) and global energy evaluation (energy efficiency criterion) was required for sizing objective. The concept of equivalent temperature can meet the first requirement as it characterises accurately the heat exchange between the exchanger wall and reactive medium. In the domain of global model, such a concept was revealed to be better for the hypothesis based on the uniform temperature, and allows the parameters to be controlled in a relatively precise way particularly powers and degree of conversion. The application of equilibrium temperature was validated by experiments, and \(k_s\) and \(k_d\) were correlated with the performance of heat exchanger and characteristics of salt reactant and chemical reaction as expressed in Eq. (19):

\[
k = \frac{a}{n_{\gamma} \Delta H_{l}}
\]  

(19)
where \( a \) (W/K) is the local exchange coefficient per volume unit of the reactant \([28, 29]\) and equals to the product of heat transfer coefficient and heat transfer area \( (U_{sw}S_{sw}) \); \( n_i \) is the molar number of the salt, \( \gamma \) is the stoichiometric coefficient, \( \Delta H_r \) is the reaction enthalpy. Goetz and Llobet \([28]\) and Lépinasse et al. \([29]\) employed the same method to obtain the values of the local volumetric exchange coefficient according to their experimental results (7.85 L reactor \([28]\) and 1.15 L reactor \([29]\)), as given in Table 7 (molar number of salt per volume unit of the reactant, \( N_s \), was used).

Three of the mentioned studies applied this model as a global model \([10, 27, 29]\) which treated the reactor as a lump uniform unit with an emphasis on the relevance of \( k_s \) and \( k_d \) to the geometry and heat transfer condition of the reactor. Goetz and Llobet \([28]\) discussed Iloeje et al.’s model for both local and global analysis (mass transfer limitation was ignored), and noticed that the value of the equivalent parameter \( k \) was reduced from 30 kW/(m\(^3\) K) as identified for the local volume coefficient, to 10 kW/(m\(^3\) K) determined with the global degree of conversion, which accounted for the influence of limited heat conduction through the reactant on the chemical reaction rate.

2.2.5. Huang et al.’s Model (2004) and Iwata et al.’s Model (2014)

Mazet et al. \([2]\) used a constant value to represent the Arrhenius term, as described in Section 2.2.2. Huang et al. \([30]\) determined the two parameters, \( s \) and \( E \), separately for the kinetic equation as expressed in Eq. (20) to describe the chemisorption between \( \text{SrCl}_2 \) and \( \text{NH}_3 \); meanwhile experiments were conducted on a cylindrical bulk of reactant with a volume of 1.76 L (150 mm diameter, 100 mm height, an 8 mm-diameter hole in the centre for gas diffusion) to determine the corresponding parameter values, as listed in Table 8. The parameter values were determined in a local method that coupled the kinetics and heat transfer and required the discretization of the equations in space (radial direction) and time. Huang et al.’s model of \( \text{SrCl}_2-\text{NH}_3 \) chemisorption has been used in other works as well \([31, 32]\).
Kinetic Models of Salt-Ammonia Chemisorption

\[
\frac{dx}{dt} = s_s \exp \left( \frac{-E_s}{RT} \right) (1 - x)^{m_s} \frac{P_c - P_{eq(T)}}{P_{eq(T)}}
\]  

(20a)

\[
\frac{dx}{dt} = s_d \exp \left( \frac{-E_d}{RT} \right) x^{m_d} \frac{P_c - P_{eq(T)}}{P_{eq(T)}}
\]  

(20b)

Iwata et al. [33] developed similar models for MgCl$_2$-NH$_3$ chemisorption, however, with one more parameter, an exponent was given to the pressure difference term as shown in Eq. (21). With the hypothesis of no heat and mass transfer limitation, the kinetic parameters for MgCl$_2$-NH$_3$ chemisorption, as presented in Table 9, were determined in a global approach through the comparison between simulated and experimental results on a micro-level disk reactive medium of the salt-carbon fiber composite with a 15 mm diameter and 1.2~3 mm thickness.

\[
\frac{dx}{dt} = s_s \exp \left( \frac{-E_s}{RT} \right) (1 - x)^{m_s} \left( \frac{P_c - P_{eq(T)}}{P_{eq(T)}} \right)^{n_s}
\]  

(21a)

\[
\frac{dx}{dt} = -s_d \exp \left( \frac{-E_d}{RT} \right) x^{m_d} \left( \frac{P_{eq(T)} - P_c}{P_{eq(T)}} \right)^{n_d}
\]  

(21b)

**Table 8. Values of parameters in Huang et al.’s model for SrCl$_2$-NH$_3$ chemisorption**

<table>
<thead>
<tr>
<th></th>
<th>$s_s$ (s$^{-1}$)</th>
<th>$E_s$ (J/mol)</th>
<th>$m_s$ (s)</th>
<th>$s_d$ (s$^{-1}$)</th>
<th>$E_d$ (J/mol)</th>
<th>$m_d$ (s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrCl$_2$-8/1 NH$_3$</td>
<td>0.019</td>
<td>6921</td>
<td>2.96</td>
<td>0.125</td>
<td>9000</td>
<td>3.02</td>
<td>Huang et al. [30], 2004</td>
</tr>
</tbody>
</table>

**Table 9. Values of parameters in Iwata et al.’s model for MgCl$_2$-NH$_3$ chemisorption**

<table>
<thead>
<tr>
<th></th>
<th>$s_s$ (s$^{-1}$)</th>
<th>$E_s$ (J/mol)</th>
<th>$m_s$ (s)</th>
<th>$s_d$ (s$^{-1}$)</th>
<th>$E_d$ (J/mol)</th>
<th>$m_d$ (s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCl$_2$</td>
<td>4.31E6</td>
<td>67000</td>
<td>0.65</td>
<td>1.7</td>
<td>2410</td>
<td>38800</td>
<td>0.67</td>
</tr>
</tbody>
</table>
2.2.6. Oliveira and Wang’s Model (2008)

Kinetic model of CaCl₂-NH₃ chemisorption was developed on the basis of experiments by Oliveira and Wang [34] on 226 g CaCl₂-expanded graphite composite in cylindrical shape with annular cross section. To better fit the experimental results, the authors used the ΔEQ term that is a quadratic function of both pressure and temperature:

$$
\Delta EQ = \ln \left( \frac{P}{P_{eq}(T)} \right) \left( \frac{1}{T} - \frac{1}{T_{eq}(P)} \right)
$$

(22)

Compared to the commonly used linear form of pressure/temperature difference, using the above ΔEQ term led to the calculation results that better agreed with Oliveira and Wang’s experimental data. It was explained that the ΔEQ term took into account of the existence of a pseudo-equilibrium zone. Moreover, the term in Eq. (23) was also used to represent the influence of the gas in the void space of the reactant on kinetics:

$$
N = \left( \frac{P_e}{RT \rho_m} \right)^n \rho_m
$$

(23)

where \( \varepsilon \) is the reactant porosity, \( \rho_m \) is the molar density of the salt in the bulk reactant. This term considers the ammonia as ideal gas and the exponential term \( n \) indicates how the influence changed with the gas concentration in the void space.

The complete expression of Oliveira and Wang’s model for CaCl₂-NH₃ synthesis process is the Eq. (24):

$$
\frac{dx}{dt} = k_s (1 - x)^m \left( \frac{P_e}{RT \rho_m} \right)^n \ln \left( \frac{P}{P_{eq}(T)} \right) \left( \frac{1}{T} - \frac{1}{T_{eq}(P)} \right)
$$

(24)
By adopting a relatively local approach with the measured data of three imaginary layers within the reactive medium, heat and mass transfer equations have been coupled with kinetic one to solve the equations and determine the kinetic parameters listed in Table 10.

**Table 10. Values of parameters in Oliveira and Wang’s model for CaCl₂-NH₃ synthesis**

<table>
<thead>
<tr>
<th></th>
<th>kₙ (s⁻¹)</th>
<th>m₁ (⁻)</th>
<th>n₁ (⁻)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl₂-4/2 NH₃</td>
<td>1.12E5</td>
<td>2</td>
<td>2</td>
<td>Oliveira and Wang [34], 2008</td>
</tr>
<tr>
<td>CaCl₂-8/4 NH₃</td>
<td>1.025E4</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

2.2.7. Zhong et al.’s Model (2009)

Linear Driving Force (LDF) model and Fickian Diffusion (FD) model have been also used to depict the dynamics of adsorption cycles and estimate diffusivity parameters. These two models are simplified from the Chemical Potential Driving Force model for special cases of isothermal process (uniform temperature throughout the reactive medium) at low gas pressure (Henry’s law region). Unlike the foregoing chemisorption kinetic models, the dynamics of chemical reactions are not considered in LDF and FD models. These two models have been commonly used for physical adsorption process, the impact of pressure difference on mass transfer through the pores structure and therefore on the dynamic performance of the complete adsorption system are emphasized [36].

The FD model is generally regarded as fundamentally adequate to describe pure gas adsorption/desorption kinetics for the aforementioned special cases. However, the model imposes formidable mathematical complication and requires impractically large computational time for process simulation, hampering a rapid process design under realistic conditions. On the contrary, the mathematically simple LDF model with a lumped mass transfer coefficient significantly reduces the computational time required for realistic process simulation because the detailed characteristics of a local adsorption kinetic model are lost during repeated averaging integrations of its properties needed to obtain the final process performance. The LDF model may not be valid in some conditions in which
heat transfer and chemical reaction have great effect on the sorption process. The rate of adsorption of adsorbate into adsorbent particles in the LDF model is given as [35]:

\[
\frac{dx(t)}{dt} = Y(x^* - \bar{x}(t))
\]  

(25)

where \(\bar{x}(t)\) is the average adsorbate concentration in the adsorbent particle at time \(t\), \(x^*\) is the final equilibrium adsorbate concentration in the adsorbent particle, \(Y\) is called the effective LDF mass transfer coefficient.

In favour of the simple, analytical and physical consistent form of LDF model, Zhong et al. [36] modify the original LDF model by considering chemical kinetics to predict the dynamics of BaCl\(_2\) (58.7% by weight in vermiculite matrix) and ammonia chemisorption, as expressed in Eq. (26):

\[
\frac{dx}{dt} = -\frac{1}{G \Delta P} + \frac{1}{Y(x - x_{eq})}
\]

(26)

where \(G\) is a resistant coefficient due to chemical reaction between the adsorbate and adsorbent, in Pa·s and, \(Y\) is the mass transfer diffusion coefficient in s\(^{-1}\). To identify the parameters involved in Eq. (26), the measurement of sorption curves under isothermal conditions for a small sample subjected to stepwise change in the sorbate pressure were conducted, thus the dynamics of the adsorption was mainly dominated by mass transfer rather than heat transfer. The values of \(G\) and \(Y\) were determined by the data fitting of the experimental results, as presented in Table 11. It should be noted that the isothermal condition is not consistent with real adsorption systems; on the contrary, both adsorption and desorption are driven by a temperature jump of 10~50 °C [37] at nearly isobaric conditions in real systems. More testing under the conditions of varying pressure and temperature is necessary to validate the application of this model for practical performance prediction.

| Table 11. Values of parameters in Zhong et al.’s model for BaCl\(_2\)-NH\(_3\) synthesis |
2.2.8. Li et al.’s Model (2010)

Li et al. [38] proposed synthesis and decomposition kinetic models of CaCl$_2$-NH$_3$ chemisorption shown in Eq. (27) based on their experiments on a fin structure reactor that contained about 53.6 g salt-expanded graphite composite reactant. The corresponding parameter values are given in Table 12.

\[
\frac{dx}{dt} = s_s \exp \left( \frac{E_s}{R T} \right) (1 - x)^{m_s} \frac{P_c - P_{eq}(T)}{P_c \left( \frac{T}{T_c - 273} \right)^{n_s}} \\ (27a)
\]

\[
\frac{dx}{dt} = s_d \exp \left( \frac{E_d}{R T} \right) x^{m_d} \frac{P_c - P_{eq}(T)}{P_c \left( \frac{T}{T_c - 273} \right)^{n_d}} \\ (27b)
\]

It should be noticed that the last term on the right side of the equation is a function of the local reactant temperature $T$ and constraining temperature $T_c$. This term reflects the influence of the limited heat transfer and the uneven temperature distribution through the reactant on the chemisorption kinetics.

### Table 12. Values of parameters in Li et al.’s model for CaCl$_2$-NH$_3$ chemisorption

<table>
<thead>
<tr>
<th></th>
<th>$s_s$ (s$^{-1}$)</th>
<th>$E_s$ (J/mol)</th>
<th>$m_s$</th>
<th>$n_s$</th>
<th>$s_d$ (s$^{-1}$)</th>
<th>$E_d$ (J/mol)</th>
<th>$m_d$</th>
<th>$n_d$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl$_2$-4/2 NH$_3$</td>
<td>0.00204</td>
<td>1383.24</td>
<td>2</td>
<td>4</td>
<td>0.0005</td>
<td>2385</td>
<td>2</td>
<td>4</td>
<td>Li et al. [38], 2010</td>
</tr>
<tr>
<td>CaCl$_2$-8/4 NH$_3$</td>
<td>0.0175</td>
<td>3316.95</td>
<td>6</td>
<td>-1.2</td>
<td>0.00275</td>
<td>1174.55</td>
<td>6</td>
<td>1.2</td>
<td></td>
</tr>
</tbody>
</table>
adsorbent grains (0.833 g) placed on a flat metal support to imitate a heat exchanger fin with the attempt of eliminating heat and mass transfer limitation on chemical kinetics. Kinetic equations in exponential form were used to depict the dynamics of chemisorption between BaCl$_2$-vermiculite (45:55 by weight) composite sorbent and ammonia vapor. With the hypothesis of uniform temperature and pressure within the reactive medium, the kinetic parameter was determined by fitting the following equations with the experimental results for synthesis and decomposition respectively:

\[ x = 1 - \exp(-C(T_{eq}(P) - T)t) \]  
\[ x = \exp(-C(T - T_{eq}(P))t) \]

where the constant $C$ is not dependent on pressure or temperature, and has the same expression as in Eq. (19) which is the function of heat transfer coefficient, heat transfer area and synthesis/decomposition heat associated and was calculated as around 0.000335 K$^{-1}$ s$^{-1}$ for the case studied in [39].

3. **Model Comparison and Discussion**

Different models are compared in this section for different salts. Obviously, it is almost impossible to verify the accuracy of each model/parameter due to different purpose and focus of model development as well as lack of unanimous standard on the preparation of experimental sample, size and design of testing apparatus and testing conditions. Most of reviewed models are analogical models and have modified forms on the basis of general format to more accurately represent their individual experimental cases with different reactants in different scales (micro-, meso- or macro- level) and different geometric properties under different operating conditions. As aforementioned these analogical models are only reasonably valid for the simulation of the reactor/reactant in similar
Kinetic Models of Salt-Ammonia Chemisorption

geometric structure to the reference volume under certain working conditions that are used to determine the kinetic parameters, as long as the hypothesis adopted during the model development is still satisfied.

For all studied cases in this section, assuming the used adsorbent has the bulk density of 400 kg/m$^3$ and the mass ratio between salt and supporting material is 3:1; the evaporation/condensation temperature of ammonia is given at ambient temperature of 25 °C which gives a constraint pressure, $P_c$, at 9.717 bar; while the constraint temperature for the synthesis/decomposition of different salt ammines should be designed to create sufficient equilibrium pressure drop. For all cases compared, the value of $P_c/P_{eq}$ was pre-defined as 2 for synthesis and as 0.5 for decomposition. The evolutions of degree of conversion of different salt-ammonia chemisorption using different kinetic models and different values of parameters are shown in Figure 4 to Figure 10, with large discrepancies between each other.

The grain-level model developed by Goetz and Marty [20] and Lu et al. [21] gives the quickest reactions (MnCl$_2$-6/2NH$_3$, BaCl$_2$-8/0NH$_3$, and NiCl$_2$-6/2NH$_3$) that completes within one minute. This could be explained by that the model was developed on a microscopic grain level without heat transfer limitation, but for bulk reactant the heat transfer and mass diffusion at the pellet level have evident impact on the reaction kinetics. However, in most analogical models this impact have been merged into the intrinsic characteristics of chemical kinetics because the modelling was simplified as uniform temperature and pressure within the reactive medium, or uniform temperature with mass transfer limitation, or uniform pressure with heat transfer limitation. That is also the main reason that the analogical models cannot be used to quantify the effect of particular property value of reactor/reactant on the kinetics, the reproduced kinetics represents the overall effect of various factors on the kinetics. Therefore, it can be expected that the models developed at a micro level might have faster reaction rate than that at a macro level. The modelling based on the grain-pellet concept seems to have higher accuracy and wider applicability.
for the optimal reactor/reactant design and system performance prediction when coupled with heat and mass transfer equations.
Figure 4. Degree of conversion of MnCl₂-6/2NH₃ chemisorption, (a) Synthesis; (b) Decomposition.
Figure 5. Degree of conversion of BaCl$_2$-8/0NH$_3$ chemisorption, (a) Synthesis; (b) Decomposition.
Figure 6. Degree of conversion of CaCl$_2$-8/4NH$_3$ chemisorption, (a) Synthesis; (b) Decomposition.
Figure 7. Degree of conversion of CaCl$_2$-8/4NH$_3$ chemisorption. (a) Synthesis; (b) Decomposition.
Figure 8. Degree of conversion of NiCl$_2$-6/2NH$_3$ chemisorption, (a) Synthesis; (b) Decomposition.
Mazet et al.’s model has been widely used due to its simplicity, many researchers have adopted the exact same equation form, however, the values of parameters are scattered even for the same salt, e.g., the value of $A_r$ is in the range of $10^{-3}$ to $10^{-2}$, leading to up to ten times difference on reaction rate. One of the key reasons is that different researchers have used different methods to determine the kinetic parameters, such as local, global or analytical methods, with or without consideration of heat and/or mass transfer limitation. Since the local degree of conversion are not accessible by any practical measurement means, using different calculation methods to acquire the local variation profile and the different definition of ‘local’ (the resolution of meshing for the discretization in space) also contribute to the difference. It is important to note that, although the parameters of analogical models are not associated with the physicochemical properties of the reactant, their values must be able to reflect any variation of reactivity due to differences in configuration. It is recommended to
conduct a whole set of experiments under different conditions, like different packing densities and binder/salt ratios, to determine each parameter as independently as possible.

When the basic, simplest form of Mazet et al.’s model cannot satisfactorily reproduce the measured data with hypothesis adopted, slight changes have been made to the formula to achieve better accuracy of representation, such as in Huang et al.’s model, Iwata et al.’s model, Oliveira and Wang’s model and Li et al.’s model. These models with modified terms those have none or unclear physical meanings but complicate the generic equation may have more rigorous applicability, e.g., being only valid for the study of scale changes strictly based on the reference prototype, using the exact same process design under the same conditions and the similar other system components.

CONCLUSION

In this paper/chapter, kinetic models of salt-ammonia chemisorption, including BaCl₂-8/0NH₃, CaCl₂-4/2NH₃, CaCl₂-8/4NH₃, MgCl₂-6/2NH₃, MnCl₂-6/2NH₃, NiCl₂-6/2NH₃, PbCl₂-8/3.25NH₃ and SrCl₂-8/1NH₃, have been reviewed and compared. The calculated degree of conversions using the reviewed kinetic models/parameter values showed large discrepancies, and the reasons have been discussed. The Goetz and Marty’s model and Lu et al.’s model at grain level led to the quickest reaction rate in all studied cases; nevertheless, for the simulation at pellet level, the grain kinetics should be coupled with geometric properties and heat and mass transfer characteristics of the studied reactant, and the links with the peripheral components and external heat source/sinks should be established for the system overall performance prediction and installation dimensioning. For analogical kinetic models with parameters determined through local, or global, or analytical methods, more or less the overall effect of heat and mass transfer, geometric and physicochemical properties of the reactant on the reaction rate have been merged together without clear boundary, which
reduces the applicability of those analogical model and should be avoided as much as possible to get pure kinetic of chemisorption. However, they still can be used for the study of scale changes and conditions optimization with acceptable accuracy. For individual case study, preliminary assessment of resources and information and objective identification should be conducted to choose the most suitable model for specific need.

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REFERENCES


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in a sorption heat pump cooled by a two-phase closed thermosyphon. 


