암모니아 분해를 통한 수소 촉매 생산 시뮬레이션을 위한 Takahashi 모델의 수정

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A modified form of Takahashi's microkinetic model for simulations of catalytic hydrogen production via ammonia decomposition

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Using hydrogen (H_2) produced via ammonia (NH_3) catalytic decomposition is an effective and clean alternative to fossil fuels, especially in the power generation sector, to meet carbon neutrality by 2050 [1,2]. In the NH_3 decomposition processes, ruthenium (Ru)-based catalyst can be used to significantly reduce the required high operating temperature to generate H_2 with high purity. Recently, there are many studies on H_2 generation via NH_3 decomposition using Ru-based catalysts [2-8]. However, it is still challenging in numerical investigations since sufficient chemical kinetic models are limited. To the best of authors knowledge, there exists only one detailed microkinetic model developed by Takahashi et al. [3] (referred to as Takahashi's model here) available for simulations of NH_3 decomposition using Ru-based catalysts. However, this mechanism is not applicable to ANSYS Fluent [9] or OpenFOAM [10]. This work aims to propose a modified version of the Takahashi's model (refers to as modified Takahashi's model) that is applicable to CHEMKIN-based computational fluid dynamic (CFD) platforms such as ANSYS Fluent or OpenFOAM. In the present work, only coefficients of the model for Ru/MgO catalyst are considered although the Takahashi's model was originally developed for NH_3 decomposition using Nickel (Ni) and Ru catalysts.

The Takahashi's model is based on four elementary reactions as:

$NH_3(g) + s \rightleftharpoons NH_3(a)$ (R1)

$NH_3(a) + 3s \rightarrow N(a) + 3H(a)$ (R2)

$2N(a) + 3s \rightarrow N_2(g) + 2s$ (R3)

$2H(a) \rightleftharpoons H_2(g) + 2s$ (R4)

where s is a vacant site. (g) and (a) denote gaseous species and adsorbed species on the catalytic surface, respectively. Surface reaction rates are expressed as [3]:

$$r_1 = k_1 \frac{p_{NH_3}}{p_{total}} \theta_s - \frac{k_1}{K_1} \theta_{NH_3} \quad (1)$$

$$r_2 = k_2 \theta_{NH_3} \theta_s^3 \quad (2)$$

$$r_3 = k_3 \theta_N^3 \quad (3)$$

$$r_4 = k_4 \theta_H^2 - \frac{k_4}{K_4} \frac{p_{H_2}}{p_{total}} \theta_s^2 \quad (4)$$

$$K_1 = \frac{k_1}{k_{-1}} \quad (5)$$

$$K_4 = \frac{k_4}{k_{-4}} \quad (6)$$

$$\theta_s = 1 - \theta_{NH_3} - \theta_N - \theta_H \quad (7)$$

where k_i and K_i (i = 1-4) are the kinetic constants for forward reactions and equilibrium constants, θ_i fractions of site species. The detailed expression of k_i and K_i as well as their coefficients can be found in [3].

The reasons why Takahashi's model cannot be used in ANSYS Fluent (i.e., CHEMKIN-based CFD platform) are its surface reaction rate form (Eqs. (1)-(6)) and dimension of the kinetic constants, k_i, differ from those in ANSYS Fluent. Particularly, the kinetic constants for surface reaction rates in ANSYS Fluent are in mol/m^2-s [9] while it is in $mol/g_{catalyst}$-s in Takahashi's model (see the Table 1 in [3]).

To overcome the problem, we propose a modified model for which the chemical reactions should be rewritten such that all of them are forward reactions as follows since ANSYS Fluent does not support backward surface reactions:

$NH_3(g) + s \rightarrow NH_3(a)$ (R1′)

$NH_3(a) + 3s \rightarrow N(a) + 3H(a)$ (R2′)

$2N(a) \rightarrow N_2(g) + 2s$ (R3′)

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$2H(a) \rightarrow H_2(g) + 2s$ (R4′)

$NH_3(a) \rightarrow NH_3(g) + s$ (R5′)

$H_2(g) + 2s \rightarrow 2H(a)$ (R6′)

Then, the rates of reactions (R1′)-(R6′) can be expressed in a CHEMKIN-based form by introducing a new coefficient, $coeff$, as:

$$r_1 = coeff * \frac{1}{\sum C_j} k_1 C_{NH3} \theta_s \rho_{site} \quad (1')$$

$$r_2 = coeff * k_2 (\theta_{NH3} \rho_{site})(\theta_s \rho_{site})^3 \quad (2')$$

$$r_3 = coeff * k_3 (\theta_N \rho_{site})^2 \quad (3')$$

$$r_4 = coeff * k_4 (\theta_H \rho_{site})^2 \quad (4')$$

$$r_5 = coeff * k_5 \theta_{NH3} \rho_{site} \quad (5')$$

$$r_6 = coeff * \frac{1}{\sum C_j} k_6 C_{H2} (\theta_s \rho_{site})^2 \quad (6')$$

where C_j is molar concentration of i-th species, ρ_{site} the site density of catalyst. It is of importance to note that the dimensions of kinetic constants k_i in the Eqs. (1′)-(6′) are in mol/m^2-s. The coefficients for these kinetic constants are taken from the original Takahashi's model but in the unit system as same as in ANSYS Fluent.

In the proposed model, the only unknown value is the coefficient, $coeff$. To find this value, we perform a simulation of two-dimensional (2-D) axisymmetric fixed bed catalytic reactor using ANSYS Fluent [9] with a configuration shown in Fig.1. The computational domain consists of 41,600 structured elements with the uniform grid size of 0.5 mm in both axial and radial directions. This test case has been conducted computationally by Takahashi et al. [4]. Detailed descriptions of the test case can be found in [4]. It is of importance to note that heat transfer models also play a critical role in the simulation of the catalytic fixed bed reactor. In the present work, all sufficient heat transfer models as mentioned in [4] have also been implemented using user-defined functions (UDFs) in ANSYS Fluent.

Finally, using try-and-error method to match the conversion rate of NH_3 to H_2 in the simulation adopted the modified model with the benchmark data in [4], $coeff = 0.3$ is found to be sufficient to simulate the catalytic NH_3 decomposition processes with the considerably good accuracy compared to original Takahashi's model. Particularly, the predicted conversion rate is 12.9% in the present study while it is 14.3% in [4].

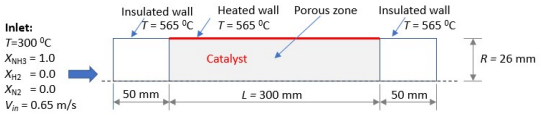

Figure 1. The configuration of a fixed bed reactor for ammonia decomposition [4].

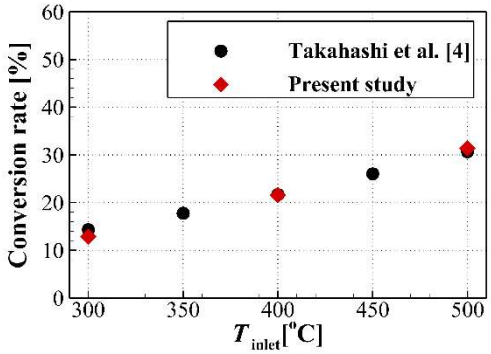

Figure 2. The validation for different inlet temperatures. Black cycle symbols are benchmark data from [4]. Red diamond symbols are data obtained in the present study.

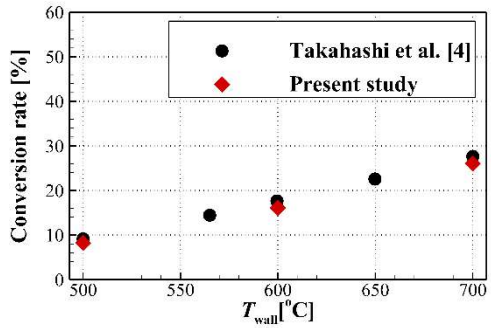

Figure 3. The validation for different wall temperatures. Black cycle symbols are benchmark data from [4]. Red diamond symbols are data obtained in the present study.

To further validate the proposed model, we also perform other simulations of the catalytic packed bed reactor having the same configuration as demonstrated in Fig. 1 with different inlet temperature and different heated wall temperature conditions [4]. As a result, the conversion rates of NH_3 to H_2 are compared

with those obtained by Takahashi and coworkers [4] as presented in Figs. 2 and 3. It can be seen from the figures that in general the results obtained from the present study are in considerably good agreement with benchmark data in [4], implying that the modified Takahashi's model is applicable to CHEMKIN-based CFD platforms with acceptable deviations compared with original Takahashi's model. Particularly, the NH_3 conversion rates predicted by modified model are very close to that of achieved by original Takahashi's model for the different inlet temperature cases (see Fig. 2) while for the cases with different heated wall temperatures the rates of NH_3 conversion showed a slightly underestimated. We conjecture that the deviations would largely originate from the differences between the adopted microkinetic model as well as the CFD framework in the present work and those in [4].

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