Modeling and simulation of ammonia hydrogen reactor based on COMSOL

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Abstract: In this paper, the optimal experimental conditions for the ammonia thermal cracking reaction with Ni-TiO$_2$-Al$_2$O$_3$ complex as the catalyst were obtained through experimental studies, and the designed ammonia to hydrogen reaction generator was modeled and the parameters of the ammonia thermal cracking reaction were simulated and analyzed by COMSOL Multiphysics software based on the experimental data. The results show that the reaction is basically completed at the inlet flow rate of 1.5 L/min, the reactor temperature range of 500 $^\circ$C-750 $^\circ$C, and the molar fraction of remaining ammonia at the outlet is about 1 wt%, which indicates the feasibility of the model and verifies the accuracy of the experiment in reverse.

1. Background

As a clean and efficient renewable energy source, hydrogen energy has been one of the research hotspots in today's energy field, which can be used as a fuel as well as promote the development of hydrogen fuel cells with good development prospects [1]. In recent years, fuel cells have received a lot of attention because of their high energy conversion efficiency and low emission advantages. And hydrogen energy is used as the main energy source of fuel cells. However, the storage and transportation of hydrogen are the main obstacles to the diffusion of fuel cell systems due to its low bulk density and boiling point, especially when operating at low temperatures [2]. Therefore, on-site hydrogen production through hydrocarbon reforming is of particular importance. Ammonia decomposition has received a lot of attention as an effective method for on-site hydrogen production. Ammonia, as a hydrogen-rich substance, contains up to 17.6% by mass of elemental hydrogen. Liquid ammonia is an ideal hydrogen carrier and has a higher bulk hydrogen density at room temperature compared to liquid hydrogen, can exist at lower pressures as well as higher temperatures, and is easier to store and transport [3].

In this paper, the principle and structure of ammonia-based hydrogen production reaction are reviewed. Based on the experimental data of ammonia thermal cracking, the designed ammonia to hydrogen reaction generator was modeled and simulated by COMSOL Multiphysics software, and the corresponding theoretical results were obtained to provide a theoretical basis for the ammonia on-site hydrogen production system.

2 Principle and structure of ammonia to hydrogen

Ammonia decomposition for hydrogen production is a simple process and plant with less investment cost, smaller size and lower energy consumption compared to water electrolysis for hydrogen production [1]. Ammonia decomposition for hydrogen production is usually based on liquid ammonia as a feedstock, which is thermally cracked in a high temperature reaction catalytic bed to produce nitrogen and...
hydrogen.

\[ 2NH_3 \leftrightarrow N_2 + 3H_2 \quad \Delta H (298K) = 94.6kJ / mol \]  

Only NH\(_3\), N\(_2\) and H\(_2\) are involved in this reaction system, and no carbon is involved in the reaction process. At the same time, the reaction is a heat absorption and molarity increasing reaction, so the high temperature and low pressure reaction conditions are more favorable for this reaction. Ammonia decomposition reaction units usually contain external decomposition, internal decomposition, and electrolysis [4,5].

3 Experimental
In this experiment, the effect of reaction temperature and ammonia inlet flow rate on the reaction of ammonia hydrogen production was mainly studied, and the hydrogen production law was evaluated by the ammonia decomposition rate.

The main raw materials used are ultra-pure ammonia (NH\(_3\)) (99.9999% purity); hydrogen (99.999% purity); carrier gas (Ar) (99.999% purity); driving gas (N\(_2\)) (99.999% purity), Wuhan Newrider Special Gas Co.

The main instruments and equipment for the experiment were mass flow meter (CS200A type), Beijing Seven Star Huachuang Flowmeter Co., Ltd; electric heating furnace reactor (YFK40X500/10QK type), Shanghai Yifeng Electric Furnace Co., Ltd; gas chromatograph (GC-9560-TCD type), Shanghai Hua Ai Chromatography Analysis Technology Co.

As shown in figure 1 for ammonia flow chart of hydrogen production by thermal cracking, hydrogen production with a certain concentration of hydrogen as reducing gas bubbled into reforming furnace in situ reduction, will be the catalyst for ammonia by the traffic control cabinet (5) into the reforming furnace complete reorganization (6), after reaction of the reformed gas by (8) into the wet type flowmeter is equipped with double valve thermal conductivity of double column (TCD) detection system of GC - 9560 gas chromatograph on-line analysis.

1. Hydrogen 2. Ammonia 3. Carrier gas 4. Drive gas 5. Flow control cabinet 6. Reforming furnace 7. Globe valve 8. Wet flowmeter 9. Gas chromatograph

Figure 1 Hydrogen production device diagram.

4 Model
Ammonia to hydrogen reactor usually involves many processes in practice, such as chemical reaction, heat transfer, flow field structure and material transfer, so several physical quantities should be coupled and calculated simultaneously in the modeling process. In this paper, we will simulate and model the reactor for ammonia to hydrogen production and analyze the performance of the obtained simulation results.

4.1 Geometric modeling
As shown in Figure 2-1, a quarter of the symmetric model structure, the model solution area is mainly divided into the stainless steel shell, porous catalyst reaction structure and gas flow channel. The overall length of the model is 0.5m, in which the stainless steel shell is 1mm thick wrapped in the outermost layer to play the role of heat transfer, and the inner Ni-Al\(_2\)O\(_3\)-TiO\(_2\) catalyst with regular pores, in which
the catalytic bed radius is 1cm and the pore diameter is 3mm.

**Figure 2 Model geometry.**

### 4.2 Physical field modeling

The model contains conditions such as ammonia inlet, reforming gas outlet, stainless steel boundary, porous gas channel, etc. In order to simplify the calculation process and improve the efficiency of the calculation a part of the reasonable assumptions on the model was constructed and calculated, involving the following basic equations.

1. The equations for the flow of free and porous media are used to describe the velocity field relationship between the reaction of ammonia and the porous catalyst.

   \[
   \rho(u_2 \nabla)u_2 = \nabla[p_s l + k] + F \\
   \rho(\nabla u_2) = 0, \quad k = \mu(\nabla u_2) + (\nabla u_2)^T
   \]

2. The equation for heat transfer in porous media is used to describe the relationship between the temperature fields of the component mixtures.

   \[
   \rho C_p \mu u \nabla T + \nabla q = Q + Q_{rad} \\
   q = -k_{eff} \nabla T, \quad k_{eff} = \theta_p k_p + (1 - \theta_p)k + k_{disp}
   \]

3. Equations for the transfer of concentrated matter are used to describe the mass transfer in convective mixtures and porous media.

   \[
   \nabla j_i + \rho(\nabla u)\omega = R_i \\
   j_i = -\rho D_i^n \nabla \omega_i + \rho \omega_j D_i^m \nabla M_i - j_{i,j} + D_i^r \nabla L \\
   D_i^m = \frac{1 - \omega_i}{\sum_i M_i}, \quad M_i = \left(\sum_i \frac{\omega_i}{M_i}\right)^{-1}, \quad j_{i,j} = \rho \omega_i \sum_k M_k D_k^n \nabla \omega_k
   \]

   Where \( \omega_i \) is the mass fraction of each component.

4. Equations for coupling free porous media flow and dense matter transfer using reactive flow. Stephens velocity:

   \[
   \rho u_i = n \sum_i (j_i + \rho u_i \omega_i n)
   \]

Mass transfer to other phases:

\[
Q_{m} = \sum R_{i,mot}
\]
The boundary conditions are summarized from the above equations by induction and modeled by COMSOL, and the boundary equations are summarized in Table 1 below.

| Boundary number | Boundary equation |
|-----------------|-------------------|
| bou.1: Inlet: $u_2 = -U_0 n$ | $-n \cdot q = \rho \Delta H u \cdot n$ |
| inflow: $\Delta H = \int_{T_{in}}^{T} C_p dT + \int_{p_{in}}^{p} \frac{1}{\rho} \frac{\rho C_p}{(1 - \alpha_T)} dp$ | $\omega_i = \omega_{0,i}$ |
| bou. 2: thermal insulation: $-n \cdot q = 0$ | heat source: $Q = Q_0$ |
| heat flux(boundary selected as stainless steel housing boundary): $-n \cdot q = q_0$ | $q_0 = h(T_{ext} - T_2)$ |
| bou. 3: No flux: $-n \cdot j_i = 0$ |
| bou. 4: Export: $[-p_2 + k] n = -p_0 n$ | Outflow: $-n \cdot q = 0$ |
| $p_0 \leq p_0$ | $-n \cdot \rho \nabla \omega_i = 0$ |
| area 5: Reaction source: $\nabla \cdot j_i + \rho (u \nabla) \omega_i = R_i$ | Reaction: $R_{w,H_2} = 3 \rho M_{H_2} \cdot rate$ |
| $R_{w,NH_3} = -2 \rho M_{NH_3} \cdot rate$ |
| area 6: $\rho C_p u \nabla T_1 + \nabla \cdot q = Q + Q_{ed}$ | solid: $q = -k \nabla T_1$ |
| $\rho C_p u \nabla T_1 + \nabla \cdot q = Q + Q_p + Q_{ed}$ | fluid: $q = -k \nabla T_1$ |

In addition, the parameters involved in this model are summarized in Table 2 below:

| Parameters | Numerical | Meaning |
|------------|-----------|---------|
| $u_{in}$   | 0.1[m/s]  | Inlet flow velocity |
| $T_{in}$   | 300[K]    | Inlet temperature |
| $T_{ht}$   | 973[K]    | Catalytic bed inlet temperature |
| $T_{sr}$   | 973[K]    | Hole temperature |
| $p_{in, sr}$ | 75[Pa]    | Differential pressure |
| $p_{ref}$  | 1e5[Pa]   | The reference pressure |
| $ht$       | 16.53[W/m²/K] | Heat transfer coefficient |
| $D_{H_2}NH_3$ | 7.83e-5[m³/s] | Diffusion coefficient |
| $D_{H_2}N_2$  | 6.89e-5[m³/s] | |
| $D_{NH_3}N_2$ | 1.98e-5[m³/s] | |
| $M_{NH_3}$  | 17.3[kg/mol] | Molar mass |
| $M_{H_2}$   | 2.016e-3[kg/mol] | |
| $M_{N_2}$   | 28e-5[kg/mol] | |
| $w_{NH_3 \text{in}}$ | 0 | Initial mass fraction |
| $w_{H_2 \text{in}}$ | 1 | |
| $H_{sr}$    | 92e3[J/mol] | The reaction enthalpy |
| $C_p_{sr}$  | 2800[J/kg/K] | The heat capacity |
| $k_{sr}$    | 0.02474[W/m/K] | Coefficient of thermal conductivity |
| $\text{visc}_{sr}$ | 9.82[Pa·s] | Viscosity |
| rate | $T_2P_{NH_3}k_0\exp(-Ea/(R_{const}T_2))$ | Reaction speed |
| $T_2 \geq 573K$ | $\max(0,\text{rate}_1) 1.5e-8$ | |
5 Results and discussion

5.1 Influencing factors on ammonia to hydrogen
Experiments were conducted to investigate the effect of different influencing factors on the effectiveness of ammonia to hydrogen production, using the ammonia decomposition rate as the evaluation index.

Figure (a) shows the effect of inlet temperature on the decomposition rate of ammonia when the inlet ammonia flow rate of catalyst bed is 3L/min. It can be seen that with the increase of inlet temperature, the decomposition rate of ammonia increases gradually. The increase of temperature is conducive to the decomposition of ammonia, but when the temperature increases to 750°C, the decomposition of ammonia reaction has been nearly complete, the increase of temperature has little effect on the decomposition of ammonia. It can be seen from the figure that the decomposition rate of ammonia gradually decreases with the increase of the flow rate. This indicates that at a lower flow rate, the longer the ammonia can stay in the catalyst, the more sufficient the reaction will be, which is more conducive to the decomposition of ammonia, but the lower flow rate will lead to too low hydrogen production. In summary, the inlet temperature of 750 oC and the ammonia flow rate of 1.5L/min were selected as the parameter Settings of the model.

5.2 Model simulation analysis
The model is constructed based on the above parameters and physical field equations, and its parameters are simulated, and the simulation results are as follows.

Figure 4 shows the simulation results of gas velocity of the model. As can be seen from the figure, the gas flow rate in the catalyst hole can reach 1.8m/s.
Figure 4 Model gas flow rate simulation results.

Figure 5 shows the simulation results of temperature distribution inside the model reactor. When the inlet temperature is set to 750°C, the temperature inside the hole changes significantly, and the inlet temperature is close to 800°C and gradually decreases, and the temperature difference is around 200°C. The temperature of the catalytic bed decreases gradually from the shell to the center line, and the temperature difference is also about 200 °C, and the whole reactor is in a high temperature state.

Figure 5 Model temperature simulation results.

Figure 6 shows the simulation results of the residual ammonia mole fraction of the model. From the figure, it can be seen that the remaining ammonia molar fraction at the outlet is 1 wt%, indicating that the basic reaction is completed, which is consistent with the experimental data.
Figure 6 Molar fraction of residual ammonia in the model.

6 Conclusion
In summary firstly, the feasibility of the reaction was firstly verified by experiments, and the most appropriate experimental conditions were obtained for the study of different factors, which provided a great reference value for the establishment of the reactor model. As can be seen from the simulation results, under the condition of inlet flow of 1.5L/min, the temperature range of the reactor is 500-750 °C, and the mole fraction of remaining ammonia at the outlet is about 1wt%. The reaction is basically completed, which indicates the feasibility of the model and verifies the accuracy of the experiment.

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Reference
[1] An E K, Yang X and Song X. Application of ammonia as hydrogen rich carrier and fuel[J]. Energy technology, 2008, 29(04):209-211+239.
[2] Okura K, Okanishi T, Muroyama H, et al. Promotion effect of rare-earth elements on the catalytic decomposition of ammonia over Ni/Al2O3 catalyst[J]. Applied Catalysis A General, 2015, 505:77-85.
[3] Lamb K E, Dolan M D and Kennedy D F. Ammonia for hydrogen storage: A review of catalytic ammonia decomposition and hydrogen separation and purification[J]. International Journal of Hydrogen Energy, 2019, 44(7):3580-3593.
[4] Sebastien E G and Mehrdad E, Ammonia Hydrogen Carrier for Fuel Cell Based Transportation ESEA[D]. Texas A&M University. 2003.
[5] Tian H. Preparation of hydrogen from liquid ammonia by electrochemical decomposition[D]. Yangzhou university, 2016.
[6] Chellappa A S, Fischer C M and Thomson W J. Ammonia decomposition kinetics over Ni-Pt/Al2O3 for PEM fuel cell applications[J]. Applied Catalysis A General, 2002, 227(1-2):231-240.