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Supporting Information

for

Modeling-aided coupling of catalysts, conditions, membranes, and reactors for efficient hydrogen production from ammonia

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1. Expanded dataset

The experimental dataset comprises three sets: (i) kinetic data; (ii) membrane data without reaction; and (iii) membrane reactor experiments. These are summarized in **Table S1** and explained in more detail in Sections 1.1, 1.2, and 1.3 of this document, respectively.

Set no.	Reactor	Catalysts	N	Target variable	Parameters to fit
i	Non-membrane	Ru-K/CaO	95	X _{NH3}	$k_0, E_a, a and b$
	Non-membrane	Co-Ba/CeO ₂	95	X _{NH3}	$k_0, E_a, a and b$
ii	Membrane	N/A	55	R _{H2}	J ₀ , E _{a,J}
iii	Membrane	Co-Ba/CeO ₂	56	$X_{\rm NH3}$ and $R_{\rm H2}$	U

Table S1. Different sets for parameter estimation.

1.1. Kinetic data (set i)

Tests were performed using a PID Microactivity Reference system to obtain the kinetic experimental data. The experiments were performed in a wide range of temperatures (250 to 550 °C), pressures (1 to 40 bar), and space times (0.2 to 6 g_{cat} h mol⁻¹) by maintaining the amount of catalyst (200 mg, pelletized between 300 and 500 µm and diluted with 2 g of SiC) constant. The flow rates of NH₃, H₂, N₂, and Ar were controlled using dedicated mass flow controllers to explore the effects of the partial pressures of the reactants and products. Specifically, the partial pressures of NH₃ (0.05–1 bar), H₂ (0–0.75 bar), and N₂ (0–0.25 bar) were achieved by ensuring constant total flow rates and using argon as the balancing gas.

Reaction products were analyzed in an online gas chromatograph (3000 A Micro Gas Chromatograph Gas Analyzer, Agilent) equipped with thermal conductivity detectors using He as the internal standard (2 mL min⁻¹). One channel equipped with a PLOTU pre-column/Molsieve column using Ar as the carrier gas was used to detect N_2 and H_2 , and a second channel with a PLOTU column and He was used as the carrier gas to detect N_3 . The isothermal CPBR used for the kinetic experiments is a standard Autoclave Engineers design for a packed-bed system with an inner diameter (id.) of 9 mm and outer diameter (od.) of 12 mm, a catalyst support as a frit, and internal temperature measurements of the catalyst bed.

Figure S1 shows the NH₃ conversion for the Ru-K/CaO catalyst under all experimental conditions. **Figure S2** shows the same information for experiments performed with the Co-Ba/CeO₂ catalyst.



Figure S1. Catalytic performance for Ru-K/CaO catalyst. Effects on NH₃ conversion based on (a) temperature and pressure; (b) space time; (c) NH₃ partial pressure in the feed; (d) H₂ partial pressure in the feed. Conditions: $W_{cat} = 0.2$ g; $F_{NH3;0} = 30$ NmL min⁻¹; P = 1 bar.



Figure S2. Catalytic performance for Co-Ba/CeO₂ catalyst. Effects on NH₃ conversion based on (a) temperature and pressure; (b) space time; (c) NH₃ partial pressure in the feed; (d) H₂ partial pressure in the feed. Conditions: $W_{cat} = 0.2$ g; $F_{NH3;0} = 30$ NmL min⁻¹; P = 1 bar.

1.2. Membrane experiments with no reaction (set ii)

The CPBMR module was supplied by GaoQ Functional Materials Co., Nanjing, China, and consisted of a Pd-Au alloy membrane (id. = 8 mm; od. = 12 mm; effective membrane area = 70 cm²; membrane thickness = 8 μ m; Au content = 15 wt%) in a stainless-steel module with shell tube geometry, where the shell and tube sides were the catalytic bed and permeate reactor sides, respectively. The thin Pd-Au alloy layer was supported on the external surface of a porous ceramic tube. To determine n, J₀ and E_{a,J}, permeation tests were performed using different H₂/N₂ feed mixtures and the CPBMR module without catalyst load at different operating temperatures (350–500 °C); inlet flow rates (100–4000 NmL min⁻¹) and feed pressures (4–9 bar). **Figure S3** shows the hydrogen recovery for all experiments performed.



Figure S3. Temperature effect on H₂ recovery for non-reactive membrane experiments for (a) $F_{T,0} = 1000 \text{ NmL min}^{-1}$ and $P_f = 4 \text{ bar}$; (b) $x_{H2} = 0.75$ and $P_f = 4 \text{ bar}$; (c) $F_{T,0} = 1200 \text{ NmL min}^{-1}$ and $x_{H2} = 0.5$ (d) $F_{T,0} = 4000 \text{ NmL min}^{-1}$ and $x_{H2} = 0.75$. All experiments were performed at $P_p = 1$ bar.

1.3. Membrane reactor experiments (set (iii))

Two different catalyst loadings were used (2 and 10 g) in the CPBMR to explore a wide range of operating conditions. The catalysts were loaded in the annular space together with inert SiC in the weight ratio of 2: 1. NH₃ was fed onto the shell side at the top of the reactor to generate H₂, which then permeated through the Pd layer towards the center of the reactor across the entire length of the membrane/reactor. The permeated H₂ exited at the top of the reactor, while the remaining gases (N₂ and unreacted NH₃) flowed down the reactor length and exited at the bottom. Gases from the two sides of the reactor were then analyzed online using two micro gas chromatographs with identical configurations, as previously noted. **Figure S4** shows NH₃ and H₂ recovery obtained for the explored experimental conditions.



Figure S4. Ammonia decomposition in a CPBMR using Co-Ba/CeO₂ catalyst (experimental data). NH₃ conversion in terms of (a) temperature; (b) space time and (c) feed pressure; and H₂ recovery in terms of (d) temperature; (d) space time and (e) feed pressure. Conditions: $F_{NH3,0} = 100 \text{ NmL min}^{-1} (2 \text{ g}_{cat})$; $F_{NH3,0} = 300 \text{ N mL min}^{-1} (10 \text{ g}_{cat})$; $T_0 = 485^{\circ}$ C; $P_f = 4$ bar and $P_p = 1$ bar.

For the experiments performed with 10 g of the catalyst, temperature profiles were measured both inside the catalytic bed and in the outer side of the reactor wall. These experiments enable correlation of the initial temperature with the temperature wall set point and the temperature wall profile.



Figure S5. Experimental temperature profiles outside and inside the CPBMR. Setpoint of the wall temperature is (a) 350, (b) 400, (c) 450, (d) 485, (e) 500, and (f) 550 °C. All experiments were performed under the same conditions: $W_{cat} = 10$ g; $P_f = 4$ bar and $P_p = 1$ bar.

2. Pressure drop profiles

The pressure drop along the reactor was evaluated for most representative simulation conditions. It was found to be below 1 % for all cases.



Figure S6. Pressure drop for CPBMR as function of (a) dimensionless length of reactor; (b) Pe number; and (c) pressure ratio. Conditions: $Da_0 = 1$; $Pe_0 = 0.05$; $P_r = 4$ bar; $P_p = 1$ bar; $T_w = 400^{\circ}$ C; $T_0/T_w = 1$; $\alpha_{H2/NH3} = 10^5$; $\alpha_{H2/N2} = 10^5$; a = 0.5; b = -0.75; n = 0.5; $St = \infty$.

3. Combined effect of k_0 and E_a



Figure S7. Contour plots for NH₃ conversion as a function of pre-exponential factor (k₀) and catalyst activation energy (E_a) for a (a) non-membrane reactor and (b) membrane reactor. Values reported in the literature are at scale. Simulation conditions: Pe₀ = 0.05 (membrane reactor); Pe₀ = 500 (non-membrane reactor); W/F = 22 g_{cat} h mol⁻¹; St = 100; P_r = 10; P_p = 1 bar; T₀/T_w = 1; Tw = 400 °C; $\alpha_{H2/NH3} = 10^5$; $\alpha_{H2/NH3} = 10^5$; a = 0.5; b = -0.75; n = 0.5; k₀ = 10¹¹ mol h⁻¹ g_{cat}⁻¹; E_{a,J} = 25 kJ mol⁻¹.