Importance of Reaction Mechanism Involved in Design of the Catalyst and the Reactor for Future Ammonia Synthesis

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NH3 will be produced from natural gas with CCS (brawn ammonia) or renewable energy (green ammonia) in the quite near future.

Feature of green ammonia production:
1. Use of water electrolysis; Less size effect of the unit
2. Unsteady hydrogen production; tough process and catalyst (Ru)
3. Independent production of N2 and H2; use of kinetic knowledge in catalysis
4. Use of NH3 absorber material for separation
5. Cheap electric power: no use of steam

**Low H\textsubscript{2} inhibition on Ru/CeO\textsubscript{2}**

**SMSI:** Strong Metal Support Interaction (support oxide partly reduced)
Proposed mechanism of ammonia synthesis on Ru/CeO₂ (reduced at high temp) and Ru-CsOH/MgO

CeO₂ is partly reduced (SMSI) and delivers electron to Ru

CsOH sticks to Ru and delivers electron to Ru
Mechanism and the rate of catalytic ammonia synthesis

\[ \text{N}_2 + 2 \ast \rightarrow 2\text{N(a)} \quad (1) \quad \text{rate determining step} \]
\[ \text{H}_2 + 2 \ast \rightarrow 2\text{H(a)} \quad (2) \]
\[ \text{N(a)} + \text{H(a)} \rightarrow \text{NH(a)} + \ast \quad (3) \]
\[ \text{NH(a)} + \text{H(a)} \rightarrow \text{NH}_2 (a) + \ast \quad (4) \]
\[ \text{NH}_2 (a) + \text{H(a)} \rightarrow \text{NH}_3(a) + \ast \quad (5) \]
\[ \text{NH}_3(a) \rightarrow \text{NH}_3 + \ast \quad (6) \]

\[ \text{N(a)} + 1.5\text{H}_2 = \text{NH}_3 + \ast \quad (7) \]

The equilibrium constant in Eq. (7), \(1/K_d\), is expressed as:
\[ 1/K_d = (1-\theta_N)P_{\text{NH}_3}/\theta_N P_{\text{H}_2}^{1.5} \quad (8) \]
\[ (1-\theta_N) = 1 / (1+ K_d P_{\text{NH}_3}/ P_{\text{H}_2}^{1.5}) \quad (9) \]

Thus, the synthesis rate can be expressed as a function of the \(\text{N}_2\), \(\text{H}_2\), and \(\text{NH}_3\) pressure, as follows:
\[ r_1 = k_1 P_{\text{N}_2} (1-\theta_N)^2 = k_1 P_{\text{N}_2} (1+ K_d P_{\text{NH}_3}/ P_{\text{H}_2}^{1.5})^{-2} \quad (10) \quad \text{for Fe catalysts} \]
\[ r = k_1 P_{\text{N}_2} (1+ K_d P_{\text{NH}_3}/ P_{\text{H}_2}^{1.5} + K_2 P_{\text{H}_2}^{0.5})^{-2} \quad (11) \quad \text{for Ru catalysts} \]
Model kinetics and mechanism of NH₃ synthesis on Fe or Ru


\[ R = kP_{N_2}(P_{N_2}^*)^{-0.5} \]

\[ = kP_{N_2}(\frac{P_{H_2}^3}{P_{NH_3}^2})^{0.5} \]

Ammonia inhibition

Hydrogen inhibition
N2 + 3H2 → 2NH3

(H2/N2=3) gas is supplied as a whole, but we can control the reactor inlet concentration with (H2/N2=1).

Catalyst setting

Ru/CeO2

Ru-CsOH/MgO

H2 conv. 50%
Gas conv. 20%
NH3 synthesis from renewable energy: proposed unit

Excess N2 operation at first

O2 reserve

Air

P Swing

N2

0.5/6

Pump

H2

1.5/6

Electrolysis

H2O

H2 reserve

1.5/6

Pump

Ru/CoO2

Ru-CsOH/MgO

Reactor

2.5/6, 1.5/6, 1/6

Absorber separator

Alkali earth halides

Absorber separator

Alkali earth halides

NH3 reserve

1/6
Ammonia reversible absorption to CaCl_{2-x}Br_{x} (Liu, Aika; 2002)

Reversible absorption temp: 298K
●: Absorption isotherm
▲: Desorption isotherm

CaCl_{2}, CaClBr, CaBr_{2}

Anion mixed Ca halide shows intermediate character of those pure compounds

Reversible ammonia absorption on CaCl$_{2-x}$Br$_x$ (Liu, Aika 2002)

NH$_3$ reversible absorption temp: 298K
- : Absorption isotherm
▲: Desorption isotherm

CaCl$_1.33$Br$_{0.67}$, CaClBr, CaCl$_{0.67}$Br$_{1.33}$

Absorbs much amount of NH$_3$ below 60kPa, desorbs NH$_3$ above 10kPa reversibly.

⇒ Pressure swing separation of NH$_3$ is possible under mild condition.
Ammonia-halogen exchange character is changed because the change of electric field and/or structure around Ca ions. > Controls NH3 absorption pressure.