Abstract #540411

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

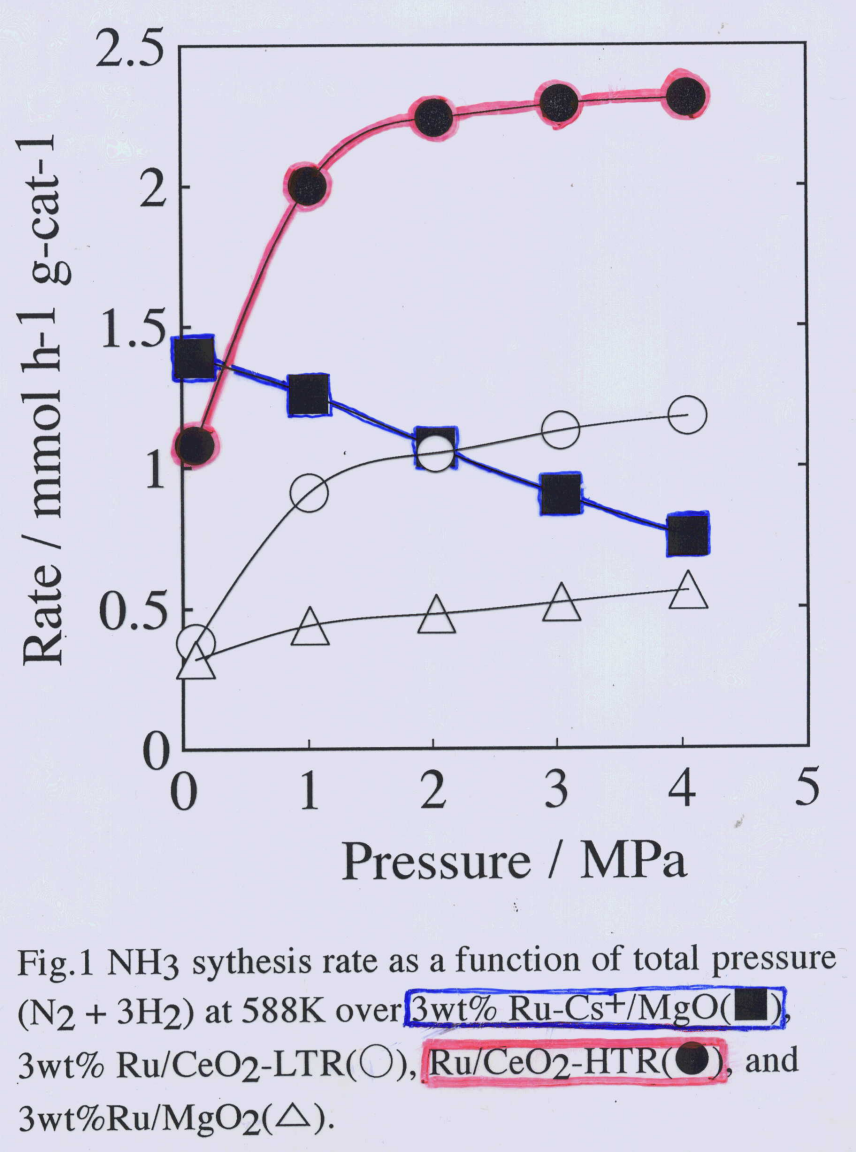


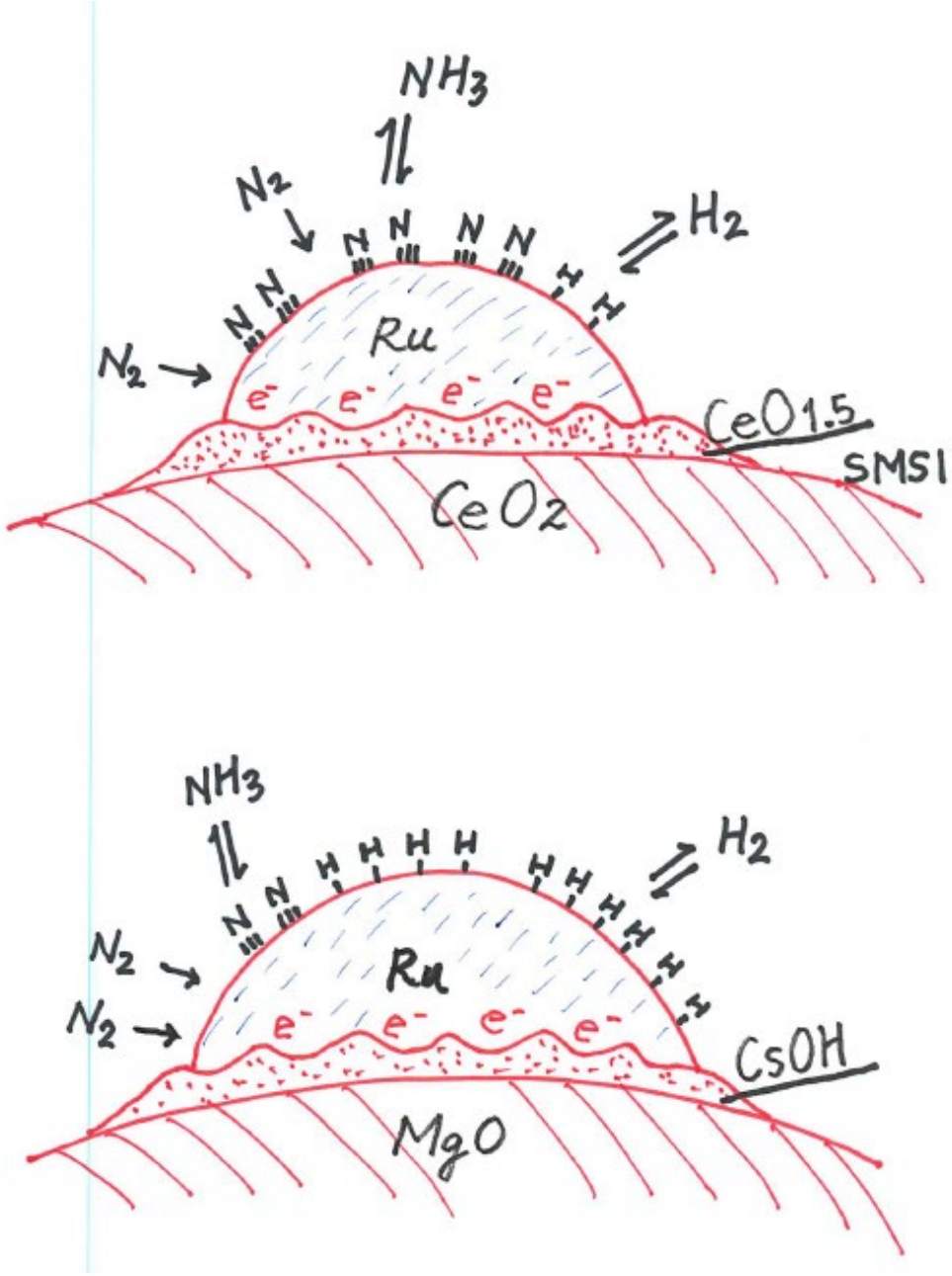
Fig.1 NH_3 sythesis rate as a function of total pressure ($N_2 + 3H_2$) at 588K over 3wt% Ru-Cs+/MgO(■), 3wt% Ru/CeO_2-LTR(○), Ru/CeO_2-HTR(●), and 3wt%Ru/MgO_2(△).

Y. Niwa and K. Aika, *J. Catal.*, 162, 138-142 (1996).

Low H_2 inhibition on Ru/CeO_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

$N_2 + 2* \rightarrow 2N(a)$ (1) rate determining step

$H_2 + 2* \rightarrow 2H(a)$ (2)

$N(a) + H(a) \rightarrow NH(a) + *$ (3)

$NH(a) + H(a) \rightarrow NH_2(a) + *$ (4)

$NH_2(a) + H(a) \rightarrow NH_3(a) + *$ (5)

$NH_3(a) \rightarrow NH_3 + *$ (6)

$N(a) + 1.5H_2 = NH_3 + *$ (7)

The equilibrium constant in Eq. (7), $1/K_d$, is expressed as:

$1/K_d = (1-\theta_N)P_{NH3}/\theta_N P_{H2}^{1.5}$ (8)

$(1-\theta_N) = 1 / (1+ K_d P_{NH3}/ P_{H2}^{1.5})$ (9)

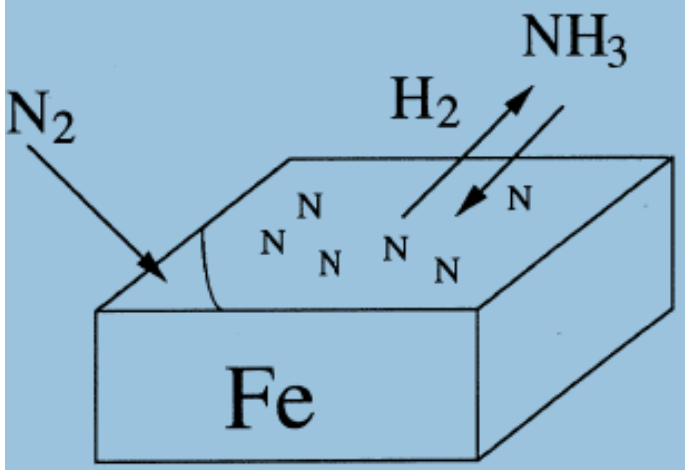
Thus, the synthesis rate can be expressed as a function of the N_2, H_2, and NH_3 pressure, as follows:

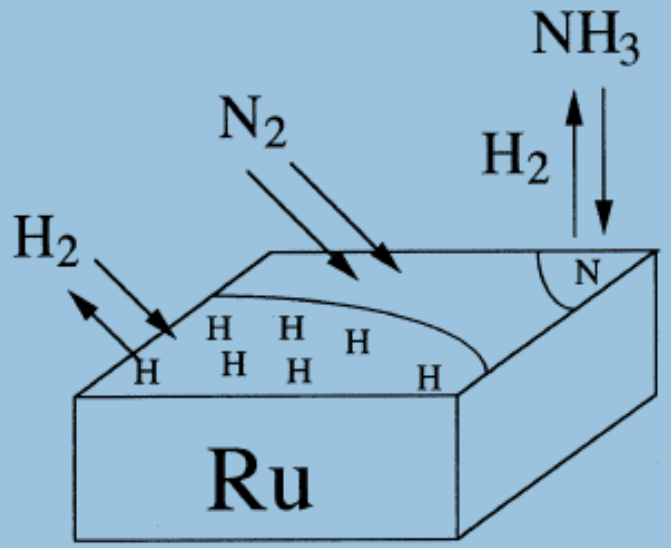
$r_1 = k_1 P_{N2} (1-\theta_N)^2 = k_1 P_{N2} (1+ K_d P_{NH3}/ P_{H2}^{1.5})^{-2}$ (10) for Fe catalysts

$r = k_1 P_{N2} (1+ K_d P_{NH3}/ P_{H2}^{1.5} + K_2 P_{H2}^{0.5})^{-2}$ (11) for Ru catalysts

Model kinetics and mechanism of NH_3 synthesis on Fe or Ru

K. Aika and A. Ozaki, *J. Catal.*, 16, 97-101 (1970).





$$R=kP_{N_2}(P_{N_2}^{*})^{-0.5}$$

$$=kP_{N_2}\left(\frac{P_{H_2}^{3}}{P_{NH_3}^{2}}\right)^{0.5}$$

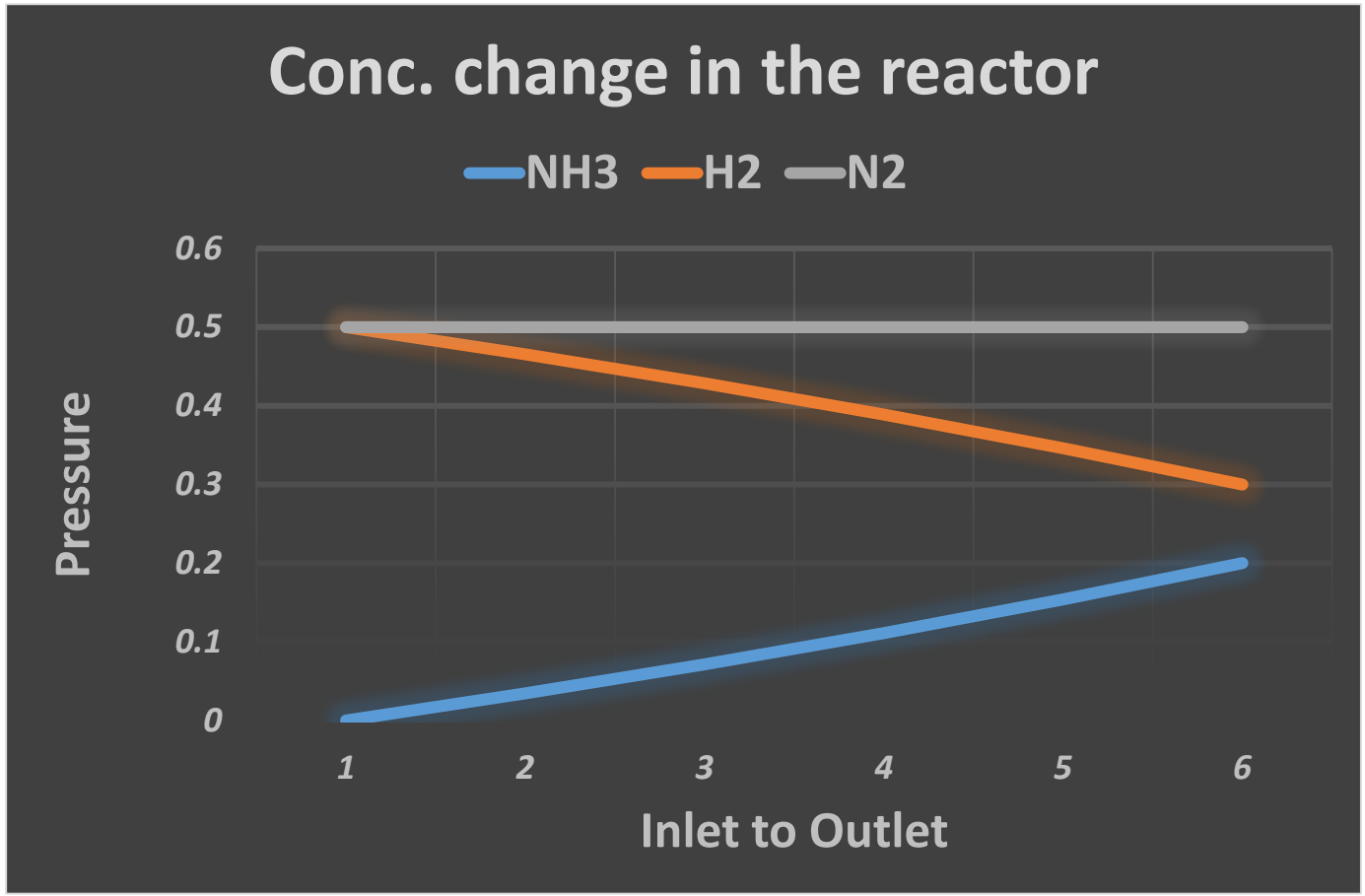
Ammonia inhibition

$$R=kP_{N_2}(P_{H_2})^{-0.5}$$

Hydrogen inhibition

$N_2 + 3H_2 \rightarrow 2NH_3$

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



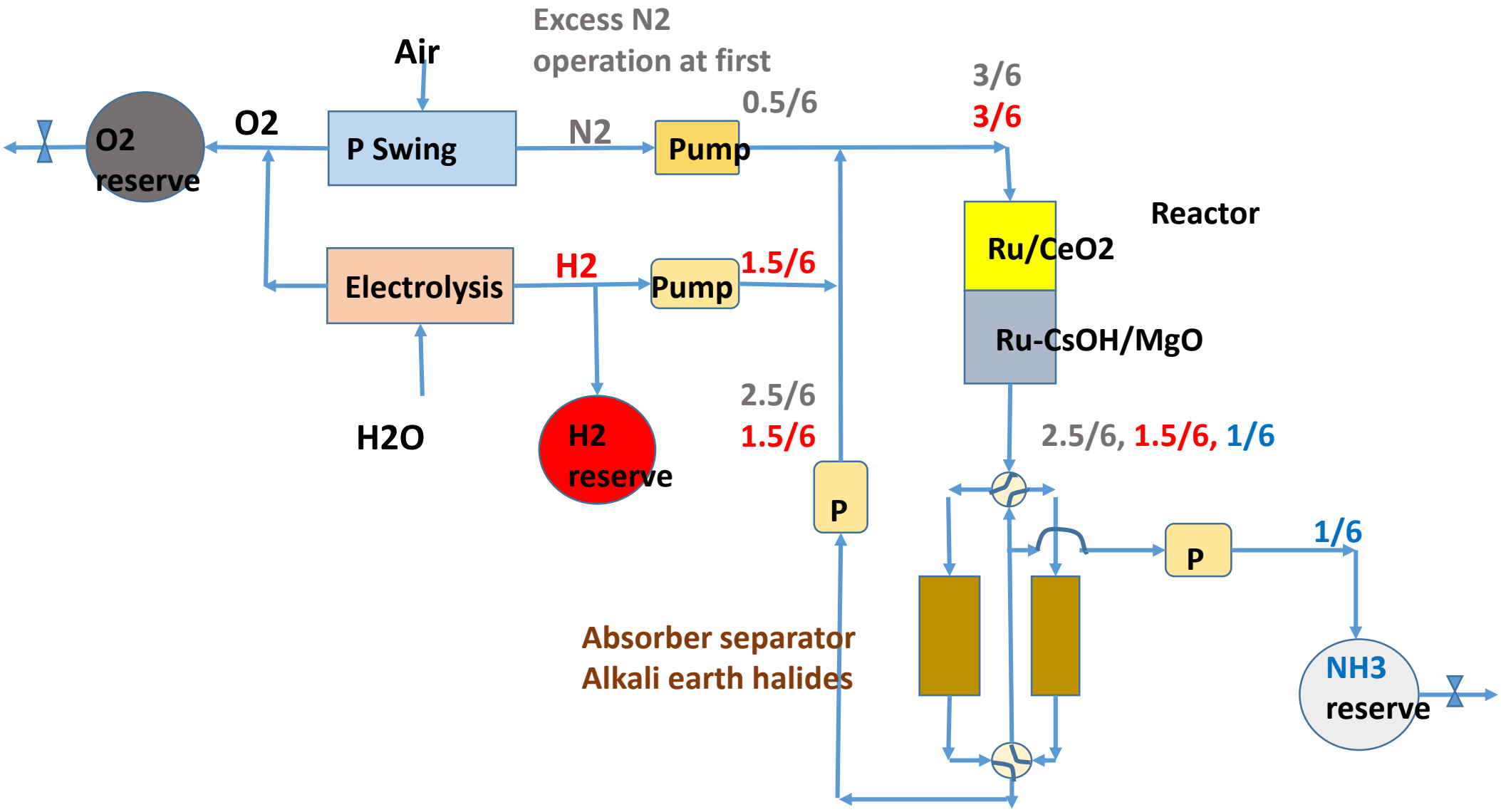
H2 conv. 50%

Gas conv. 20%

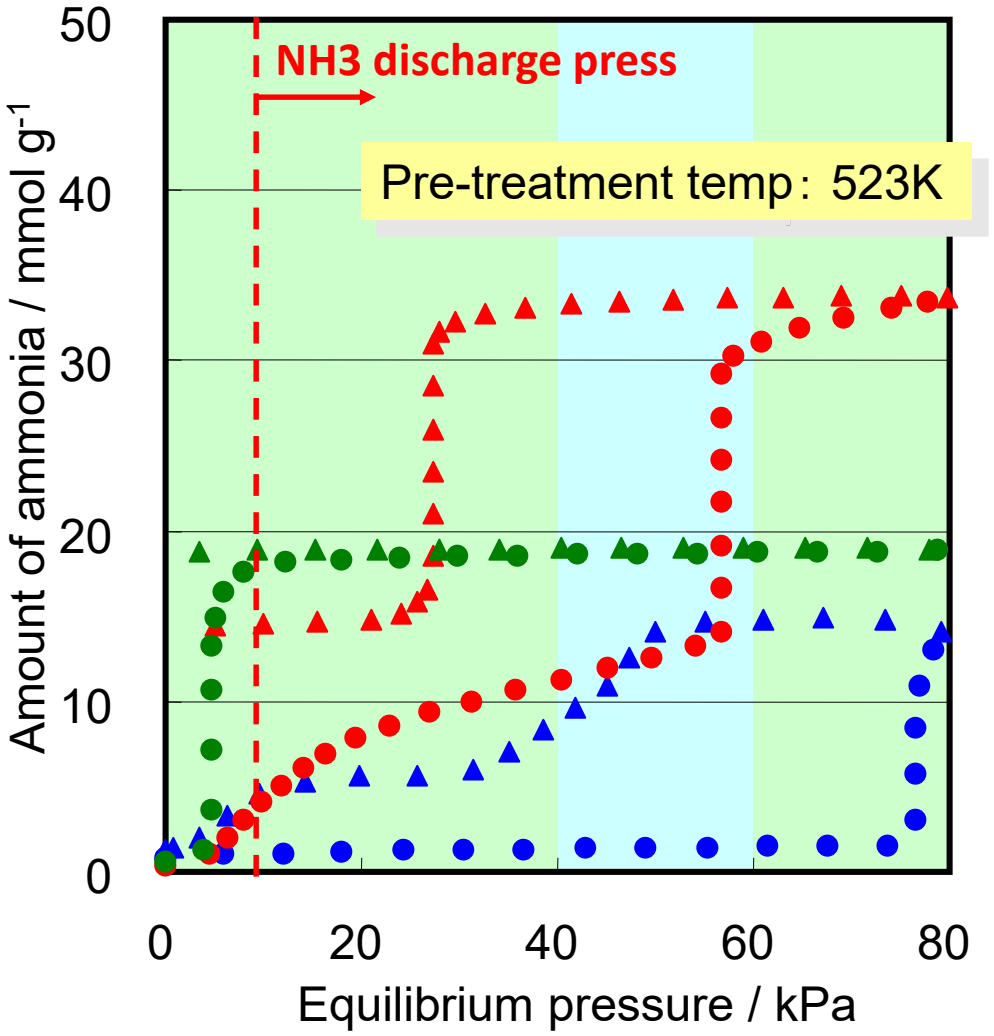
Catalyst setting

→ Ru/CeO2 → Ru-CsOH/MgO →

NH3 synthesis from renewable energy: proposed unit



Ammonia reversible absorption to $CaCl_{2-x}Br_x$ (Liu, Aika; 2002)



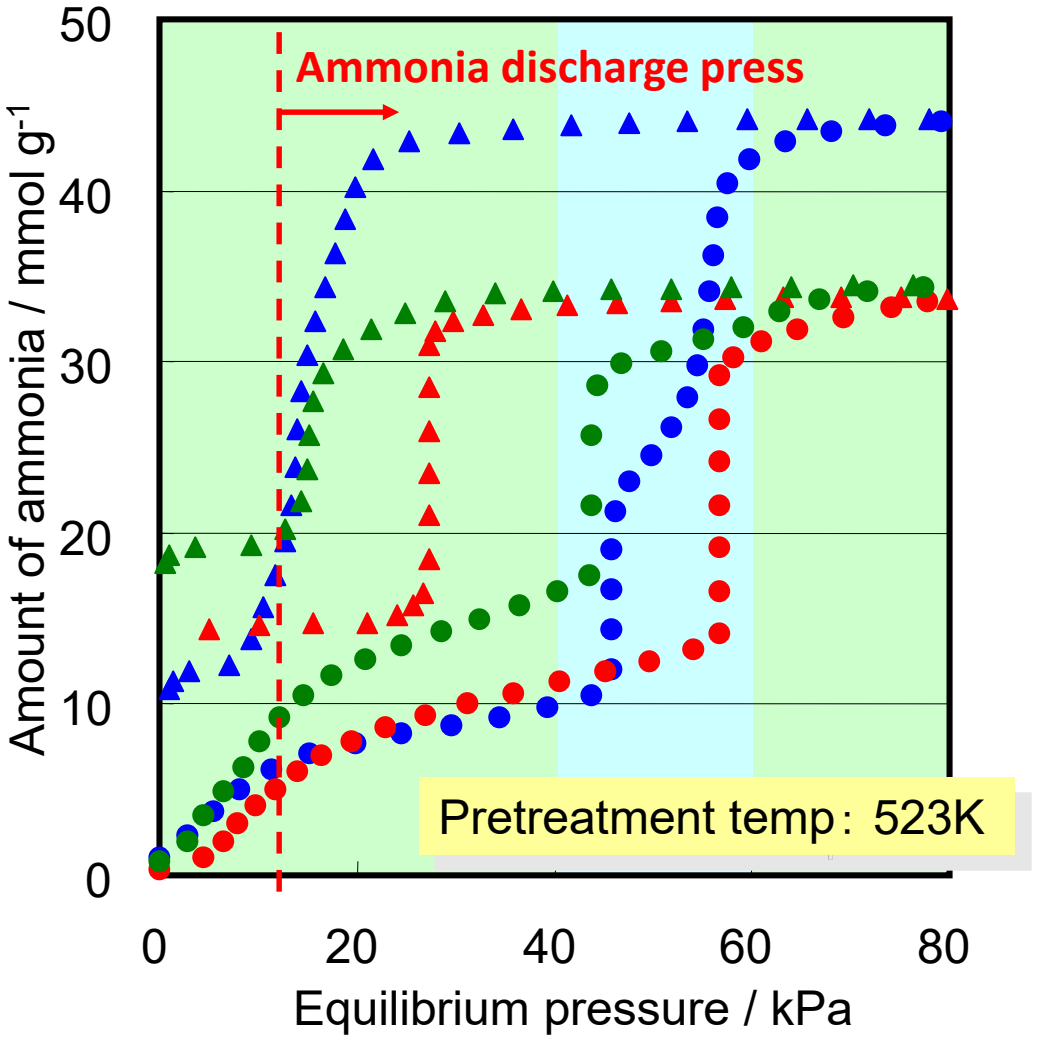
Reversible absorption temp: 298K
● : Absorption isotherm
▲ : Desorption isotherm

$CaCl_2$, CaClBr, $CaBr_2$

Anion mixed Ca halide shows intermediate character of those pure compounds

C. Y. Liu, K. Aika, Ind. Eng. Chem. Res., 43 [22], 6994-7000 (2004); ibid. 43 [23], 7484-7491 (2004).

Reversible ammonia absorption on $CaCl_{2-x}Br_x$ (Liu, Aika 2002)



NH3 reversible absorption temp：298K

●：Absorption isotherm

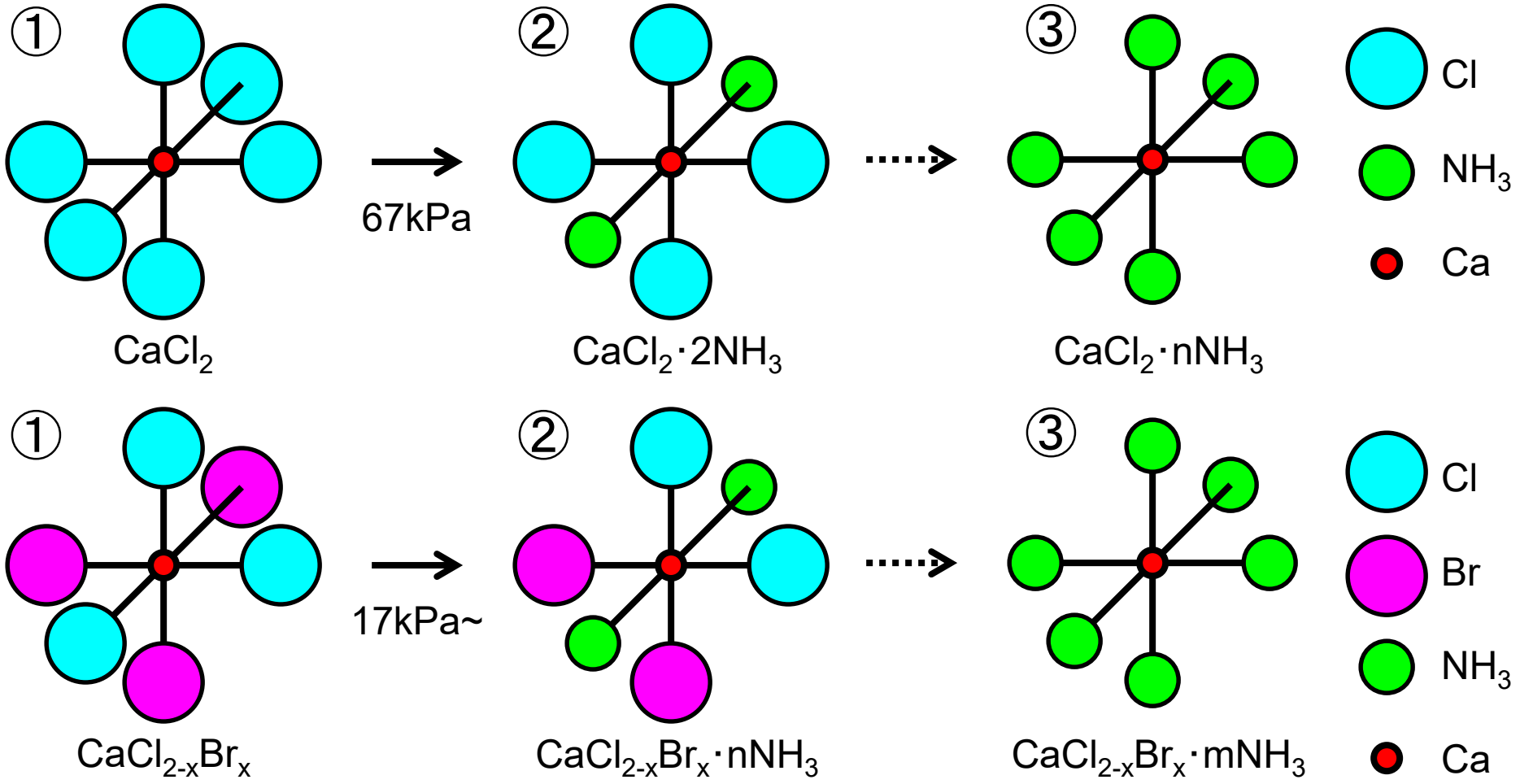
▲：Desorption isotherm

$CaCl_{1.33}Br_{0.67}$, $CaClBr$, $CaCl_{0.67}Br_{1.33}$

Absorbs much amount of NH3 below 60kPa, desorbs NH3 above 10kPa reversibly.

⇒ Pressure swing separation of NH3 is possible under mild condition.

$CaCl_{2-x}Br_x$ ammine complex formation model



Ammonia-halogen exchange character is changed because the change of electric field and/or structure around Ca ions. > Controls NH3 absorption pressure.