Synthesis and Assessment of Process Systems for Production of Ammonia using Nitric Oxide in Combustion Exhaust Gas

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Production of Ammonia using nitric oxide in combustion exhaust gas

- Industrial Ammonia Production

- NOx $\Rightarrow$ NH3 (NTA)

Approx. 250 million ton of NH$_3$ could be produced by using a half of NOx (4%) in exhaust gas from all the thermal power plants located in Japan.

$\Rightarrow$ Reutilization of produced NH$_3$ as fuel will bring about decrease in CO$_2$ emissions.
From the perspective of “Nitrogen Cycle”

Conceptual model of where interventions in the nitrogen cycle can be used to decrease the amount of reactive nitrogen (Nr) created or the amount of Nr lost to the environment.

Background for development of process systems for NH₃ production using NO in combustion exhaust gas (NTA system)

Development of new catalytic process for conversion of NO to NH₃ (NTA) : NO-CO-H₂O reaction process

Simulation analysis for effects of application of the proposed NTA system combined with lean-rich cycling operation for combustor (e.g. reciprocating engine generator)

Conclusions
Ammonia formation during catalytic NOx reduction[1]

\[
\begin{align*}
2\text{NO} + 5\text{H}_2 & \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O} \\
4\text{NO} + 4\text{NH}_3 + \text{O}_2 & \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}
\end{align*}
\]

It has been reported that complete selectivity for \(\text{NH}_3\) is difficult to achieve by means of the NO–H\(_2\) reaction under stoichiometric conditions.

Development of catalytic process for conversion of NO to \(\text{NH}_3\) (NTA) [2, 3]

\[
\text{Pt/TiO}_2 \quad \text{NO} + 2.5\text{CO} + 1.5\text{H}_2\text{O} \rightarrow \text{NH}_3 + 2.5\text{CO}_2
\]

High NO conversion and \(\text{NH}_3\) selectivity at ambient pressure and temperatures below 300 °C

Effect of the crystal type of TiO$_2$ on catalytic activity

It was shown that Pt/TiO$_2$ was higher activity than M/TiO$_2$ (M: Rh, Ir, Ru, Pd).

Anatase

Feed gas
1000 ppm NO, 3000 ppm CO, and 1% H$_2$O

- ●: Pt/TiO$_2$(A)1
- ■: Pt/TiO$_2$ (A)2
- ◆: Pt/TiO$_2$(R)
- ▲: Pt/TiO$_2$ (AR)80

※A: anatase, R: rutile

- It was observed by DRIFT (the diffuse reflectance infrared spectroscopy) that CO exhibited strong interaction with platinum on the rutile TiO$_2$.
- it was estimated that the strong interaction of CO with Pt reduced the reaction activity by comparing with Pt/anatase-TiO$_2$ catalyst.
Conceptual design of process systems for production of \( \text{NH}_3 \) using NO in combustion exhaust gas

- **Investigation, Data collection**
- **Generation of alternatives**
- **Simulation**
- **Evaluation**
  - Energy saving
  - \( \text{CO}_2 \) emissions

- **Type of combustor and its scale**

(i) Adsorption & desorption of NO
Effect of temperature and flow rate of feed gas ⇒ physical or chemical?

(ii) Conversion of NO to \( \text{NH}_3 \)
Effect of existence of \( \text{O}_2 \)

**Unified NTA reaction system**
- NO
  - Reducing agent
  - \( \text{NH}_3 \)

**Two-stage NTA reaction system**
- NO
  - Reducing agent
  - \( \text{NH}_3 \)
Adaptation of lean-rich cycling operation for combustor

\[
\text{NO} + 2.5\text{CO} + 1.5\text{H}_2\text{O} \rightarrow \text{NH}_3 + 2.5\text{CO}_2
\]

Hydrocarbon fuel

Air

Reduction

Combustion

Reduction

NO adsorption

NTA reaction

NH\(_3\)

For case of reciprocating engine generator

Lean burning

Rich burning

Excess air ratio

Time
Simulation analysis for effects of application of NTA system

- Simulation for composition of exhaust gas of combustion engine

  Zero-dimensional simulation model
  - The extended Zel’dovich mechanism for NO formation
  - Six equilibrium reactions for combustion

  Fuel (Model): Decane (T = 300 K, P = 1.5 atm)

- Search of optimum ratio of cycle time (rich-burn/lean-burn)

  Component ratio in feed to the NTA reactor was the stoichiometric ratio for NO and (CO + H2), i.e. 2 : 5.

  Operating conditions
  - Excess air ratio ($\lambda$) in rich-burn = 0.797, 0.661, 0.526
  - NO concentration in lean-burn = 500 – 2000 ppm

- Simulation of NTA process

  Equilibrium reaction model
  - Gibbs reactor model (Aspen HYSYS V9)
Influence of lean-rich cycling operation to reduction in CO$_2$ emissions in NTA system

**R1**: $2\text{NO} + 5\text{CO} + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_3 + 5\text{CO}_2$  
**R2**: $2\text{NO} + 5\text{H}_2 \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O}$

\[ T = 250 \, ^\circ\text{C} \]  
\[ C_{\text{NO}} = 2000 \, \text{ppm} \]

Reduction in CO$_2$ emissions on the basis of the NH$_3$ SCR system $\Rightarrow$ approx. 1%

※**Evaluation index**: Ratio of CO$_2$ emissions [mol] to the total heat of combustion for the consumed decane and the produced ammonia [kJ]
Influence of lean-rich cycling operation to reduction in CO$_2$ emissions in NTA system

Reduction rate for CO$_2$ emissions ($\%$) = \( \frac{(A_0 - A) \times 100}{A_0} \)

\( A = \frac{\text{Amount of CO}_2 \text{ emissions [mol]}}{\text{Heat of combustion for the consumed decane [kJ]+Heat of the produced NH}_3 \text{ [kJ]}} \)

- Influence of NO conc. under lean-bun operation
- Influence of excess air ratio under lean-bun operation

![Graphs showing influence of NO concentration and excess air ratio on CO$_2$ emissions reduction]
Simulation of reactor performance of the developed catalyst (Pt/TiO$_2$ (A))

- Kinetic analysis of NO-CO-H$_2$O reaction using Pt/TiO2 (A)

![Graphs showing kinetic analysis](image)

E = 35.1 kJ/mol

[Experimental conditions] T: 200～250 °C, $C_{NO}$: 1000-8000 ppm, $C_{CO}$: 5000-20000 ppm, $C_{H_2O}$: 6000-18000 ppm, Total flow rate: 250ml/min, Catalyst : 0.25g
Influence of reaction temperature to behavior of NTA system

R1: \[2\text{NO} + 5\text{CO} + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_3 + 5\text{CO}_2\]
R2: \[\text{NO} + (5/2)\text{H}_2 \rightarrow \text{NH}_3 + \text{H}_2\text{O}\]
R3: \[3\text{NO} + 2\text{NH}_3 \rightarrow (5/2)\text{N}_2 + 3\text{H}_2\text{O}\]
R4: \[2\text{NO} + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}\]
R5: \[2\text{H}_2 + 2\text{NO} \rightarrow 2\text{H}_2\text{O} + \text{N}_2\]
R6: \[2\text{CO} + 2\text{NO} \rightarrow 2\text{CO}_2 + \text{N}_2\]
R7: \[\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\]

\[
\begin{array}{|c|c|c|}
\hline
\text{Reaction} & \text{A(1/s)} & \text{Ea(KJ/mol)} \\
\hline
R1 & 1.76 \times 10^7 & 35.1 \\
R2 & 2.61 \times 10^{16} & 128 \\
R3 & 1.25 \times 10^{12} & 91.1 \\
R4 & 2.28 \times 10^{10} & 85.0 \\
R5 & 5.29 \times 10^7 & 69.2 \\
R6 & 1.92 \times 10^6 & 52.3 \\
R7 & 1.21 \times 10^2 & 56.7 \\
\hline
\end{array}
\]

\[r_1 = A_1 \exp \left(- \frac{E_{a,1}}{RT} \right) X_{\text{NO}} X_{\text{CO}} X_{\text{H}_2\text{O}} C_{\text{PGM}}\]
\[r_2 = A_2 \exp \left(- \frac{E_{a,2}}{RT} \right) X_{\text{NO}} X_{\text{H}_2} C_{\text{PGM}}\]

PFR Model (SimCentral 3.3)

\[C_{\text{NO}} = 2000 \text{ ppm} \]
\[\lambda = 0.5935 \]
\[t_R = 1.08 \text{ s}\]

M. Li et al.; Applied Catalysis B: Environmental, 242, 469-484 (2019)
Conclusions

- The developed NTA process using Pt/TiO$_2$ has demonstrated to be effective under low temperature condition (< 250 °C) by controlling feed of CO, by experiments and simulations.

- It was expected that positive emission of nitric oxide in combustor could enhance reduction of CO$_2$ emissions by combing with NTA reaction (NO-CO-H$_2$O reaction).

- Future work is to synthesize the NTA reaction process with a process for adsorption and concertation of nitric oxide, and to assess effects of reduction in CO$_2$ emissions for the unified system.

Type of combustor
- Flow rate
- Composition
- Temperature
- Pressure

(i) Adsorption & desorption of NO
   physical or chemical?

(ii) Conversion of NO to NH$_3$
    Effect of existence of O$_2$