

A Study of Nitrous Oxide Decomposition over Calcium Oxide

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Abstract—A study of N₂O decomposition reaction in a fixed bed reactor over bed of CaO particles has been conducted. Effects of parameters such as concentration of inlet N₂O gas, reacting temperature and content of CO₂/CO gas present in the reacting materials on the decomposition reaction have been investigated. The results showed that the conversion of N₂O decomposition was accelerated by the increase of reaction temperature, and the existence of CO, while the rate was hindered by the existence of CO₂. Heterogeneous gas solid reaction kinetics was proposed for N₂O decomposition and compared with homogeneous reaction kinetics.

Key words: N₂O Decomposition, Heterogeneous Kinetics

INTRODUCTION

One of the major environmental issues is the global warming related with the emission of CO₂, VOCs, CH₄, N₂O, etc. Nitrous oxide (N₂O), which is emitted to the environment mostly during natural processes, has been reported to have over 200 times stronger greenhouse effect than CO₂. Major source of N₂O generation is the oxidation of nitrogen components by bacteria in the soil. Therefore, destruction of the forests and land clearing, especially excessive utilization of nitrogenous fertilizer, can make the emission worse. Also, incineration of wastes and utility generation using fossil fuel can be another source [de Soete, 1994; Federal Energy Technology Center U.S. Department of Energy, 1999]. Around 10% of N₂O release is reported to be contributed by coal combustion process.

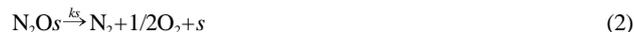
The circulating fluidized bed (CFB) coal combustion boilers showed excellent combustion and boiler efficiency. However N₂O emission in fluidized bed combustor is 30-120 ppm, which is significantly higher than that of other coal burning combustors [Åmand and Andersson, 1989; Hiltunen et al., 1991].

In the CFB power plant CaCO₃ is injected to the combustor for sulfur removal, then N₂O is decomposed over unreacted CaO and the emission is suppressed [Michael et al., 1993; Kim and Park, 1987; Kim and Rhee, 1999]. In this study the decomposition of N₂O over CaO was studied. The effects of reacting temperature and content of CO₂/CO on the decomposition reaction were analyzed, and a kinetic study considering the catalytic effect of CaO was conducted.

THEORY

N₂O decomposes on the surface of CaO, and CaO acts as catalyst [Iisa et al., 1991; Johnsson et al., 1991; Peter and Johansen,

1993; Goel et al., 1994; Lee et al., 1994; Moritomi et al., 1991]. There is intrinsic gas-solid reaction on the surface of a catalyst, and the reaction order is suggested to be first order [Shimizu et al., 1993]. The concentration of CO can be high, up to several thousand ppm, at the lower section of a CFB combustor. CO is known to promote N₂O decomposition. Few works have been done for the heterogeneous mechanism and kinetics for N₂O decomposition. Previous workers only approached with homogeneous reaction mechanism. In this work, we suggest a heterogeneous reaction mechanism using Langmuir & Hinshelwood model as follows [Smith, 1981; Satterfield, 1993]:



s is an active site on the surface of CaO where N₂O decomposition can occur, and N₂O_s describes the state of N₂O adsorption on the active site of CaO. If Eq. (2) is the rate-determining step, which means the slowest reaction, the equation of reaction can be expressed as follows.

$$r = \frac{k_s K_s [\text{N}_2\text{O}]}{1 + K[\text{N}_2\text{O}]} = \frac{k'_s K[\text{N}_2\text{O}]}{1 + K[\text{N}_2\text{O}]} \quad (4)$$

When Eq. (4) is integrated, it can be expressed as follows:

$$\frac{-\ln(1 - X_{\text{N}_2\text{O}})}{[\text{N}_2\text{O}]_0 X_{\text{N}_2\text{O}}} = \frac{k'_s \tau K}{[\text{N}_2\text{O}]_0 X_{\text{N}_2\text{O}}} - K \quad (5)$$

In Eq. (5), residence time (τ) is defined as follows:

$$\tau = \frac{W}{\rho F} \quad (6)$$

In the equation above, *W* is packing weight of CaO, ρ is the density of CaO, and *F* is the flow rate in the experimental condition.

Eq. (5) can be expressed graphically to get reaction rate constant and equilibrium constant from the slope and intercept, respectively. The activation energy and pre-exponential factor can be obtained from the rate constant (*k*'_s) of different reaction temperature by using

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the Arrhenius equation. The homogeneous reaction rate equation can be proposed by using Eq. (3). The rate is expressed as $r=k_1' [N_2O]$ and it can be integrated to make $-\ln(1-X_{N_2O})=k_1'\tau$. Thus, the heterogeneous and homogeneous equation can be compared graphically.

EXPERIMENTAL

Experimental devices used in this study consisted of reactor, flow-meter, preheater, and analyzer (Fig. 1). The reactor was made of a quartz tube with inside diameter of 2.5 cm and height of 50 cm. A quartz sintered plate was installed at the lower part of the reactor to support the CaO particles. In order to control the reaction temperature an infrared furnace with PID controller was adopted. Temperatures were measured at upper, middle, lower sections of the reactor. A flow meter was installed at the gas inlet to regulate the inlet gas. Feed gas was pre-heated up to 260 °C by a heating tape before being introduced to the reactor.

The gas concentrations of up-flow and down-flow were measured by in line gas analyzers. A mixture of CaO particles (0.3 g) and quartz beads (4 g) was filled in the reactor and then the nitrogen gas was supplied into the reactor until the reactor was heated up. When the temperature of the inside of the reactor reached the ex-

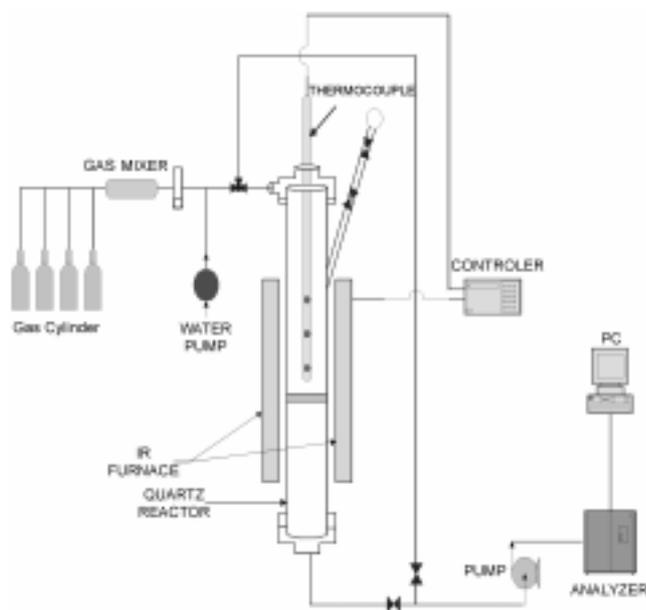


Fig. 1. Schematic diagram of experimental apparatus.

Table 1. Experimental conditions

Variables	Experimental conditions
Bed materials	CaO (0.3 g)+quartz (4 g)
Flow rate (l/min)	3.5
Temperature (°C)	800-900
N ₂ O (ppm)	200-1000
CO (ppm)	50-3000
CO ₂ (%)	0-15
N ₂	Balance

Table 2. CaCO₃ and CaO analyses

Limestone	CaO 54.14%, MgO 0.94%, H ₂ O 0.02%	
BET	Surface area (CaCO ₃) m ² /g	Surface area (CaO) m ² /g
	4.36-4.52	7.52-8.02

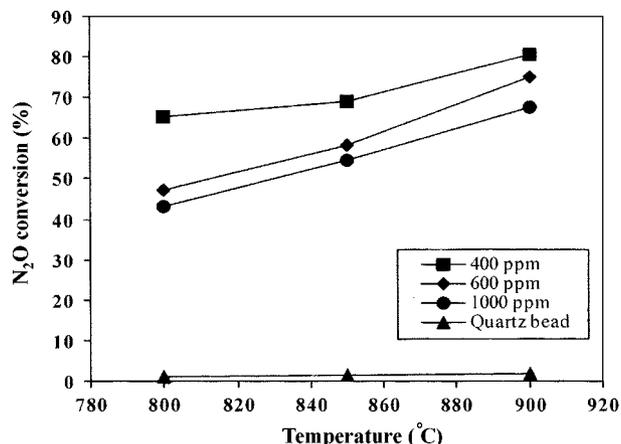


Fig. 2. Effect of temperature on N₂O decomposition.

perimental condition, the nitrogen gas was switched to sample gas. Experimental data such as reaction temperature and N₂O concentration were measured by regular intervals at the given conditions.

The experimental conditions are expressed in Table 1. CaO catalyst used in the experiment was made by calcination of the limestone from DanYang City in Korea. Its characteristics are shown in Table 2.

RESULTS AND DISCUSSION

1. Effect of Temperature

N₂O conversion according to each temperature is shown in Fig. 2. Reaction at the packed bed of CaO shows that N₂O conversion increased as the reaction temperature increased. The increase of the conversion is due to the increase of the rate constant of the surface reaction, as commented by other researchers [Iisa et al., 1991; Goel et al., 1994; Lee et al., 1994; Shimizu et al., 1993].

N₂O decomposition in quartz bed without CaO was almost nil, implying a homogeneous or heterogeneous reaction at the inert surface did not occur. Through the analysis of product gases, it was also found that N₂O was decomposed to N₂ rather than NO.

2. Effect of CO₂ Concentration

Influence of CO₂ on N₂O decomposition when CO₂ coexists is presented in Fig. 3. As the concentration of CO₂ increased, N₂O conversion was gradually decreased until the concentration of CO reached 10%. When concentration of CO₂ reached over 10%, the N₂O conversion rapidly decreased. The reduction of decomposition seemed to be related to thermodynamic property of CO₂ such that at a high concentration of CO₂, CO₂ can be absorbed into limestone. CO₂ and N₂O will compete with each other over the active site on CaO, which results in the decrease of catalyst function [Shimizu et al., 1992].

3. Effect of CO Concentration

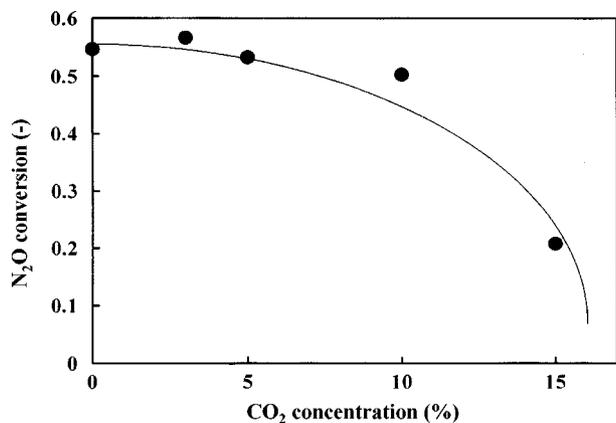


Fig. 3. Effect of CO₂ concentration on N₂O decomposition.

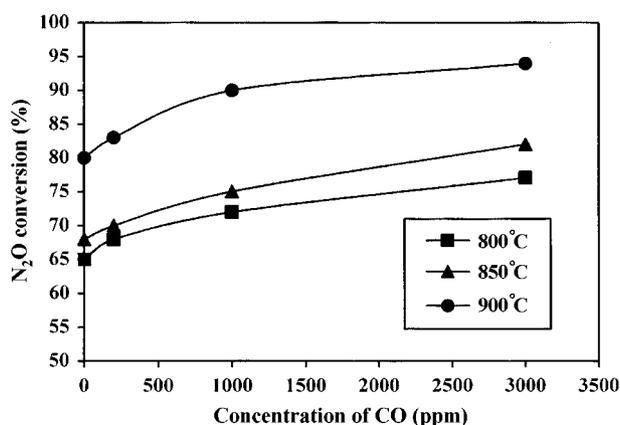


Fig. 4. Effect of CO concentration on N₂O decomposition.

N₂O conversion when CO coexists is shown in Fig. 4. When CO concentration increased from 0 to 3,000 ppm, N₂O conversion also is increased. Compared to the results of other researchers [Shimizu, et al., 1993; Johnsson and Johansen, 1994], in this study the conversion was relatively low, but the trend was similar. The reason for lower conversion of this work is associated with the different property of CaO and sample gas concentration.

In case of Johnson et al., who carried out an experiment with concentration more than 3% of CO, it was shown that more than 90% of N₂O could be decomposed using solid catalyst containing 67% of CaO [Johnsson and Johansen, 1994]. In this study, it was found that even though the extent of increase is not high, CO in low concentration promoted the N₂O decomposition.

Measurements of XRD of raw CaO and after CO/N₂O co-decomposition are expressed in Fig. 5, respectively. Fig. 5(a) is the CaO analyzed before experiment, and mostly it consisted of CaO, and a bit of impurities such as MgO. In Fig. 5(b) the characteristic peak of carbon appeared on the surface of CaO, and the smaller peak of CaO₂ is shown. In the case of CO/N₂O reaction CO is actively adsorbed on CaO surface and part of CO is converted to carbon.

The micro pore surface area was measured by BET method and is shown in Table 3. As shown in Table 3, the BET surface area almost did not change after the decomposition of N₂O alone; the surface area drastically decreased after the N₂O decomposition reac-

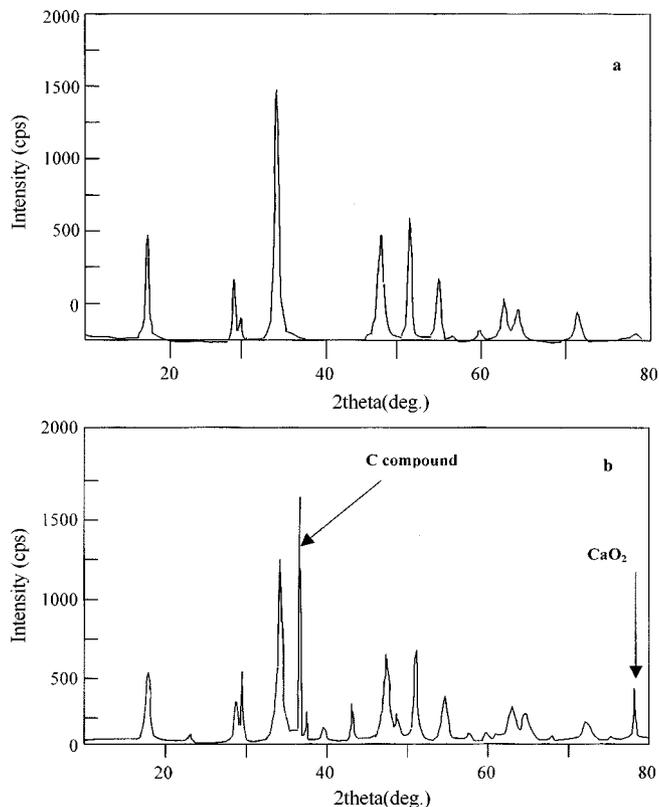


Fig. 5. Results of the XRD analysis: (a) Before experiment, (b) After experiment.

Table 3. Results of BET analysis

	Before experiment	After experiment without CO	After experiment with CO
BET surface area (m ² /g)	7.52-8.02	7.32-7.94	1.97-2.55

tion with CO. It can be concluded that in the reaction when CO coexists, physical change of CaO can be presumed to occur.

4. Kinetics Study

In this study the assumed reaction rate equation is intrinsic reaction. Therefore, we need surface concentration over particle. We measured only bulk concentration. The difference between the bulk concentration and the surface concentration can be correlated in terms of dimensionless group, i.e., in terms of j-factor [Smith, 1981]. The j-factor for mass transfer is the relationship between Sherwood number, $k_m \rho / G$, Reynolds number $d_p G / \rho$, and Schmidt number $\mu / \rho D$. The equation is as follows:

$$j_D = \frac{k_m \rho a_m}{G a_i} \left(\frac{\mu}{\rho D} \right)^{2/3} \quad (7)$$

The ratio (a_m/a_i) allows for the possibility that the effective mass-transfer area (a_m) may be less than the total external area (a_i) of the particle. Experimental reaction rate is as follows [Smith, 1981].

$$r_p = k_m a_m (C_b - C_a) \quad (8)$$

The difference between the bulk concentration and the surface

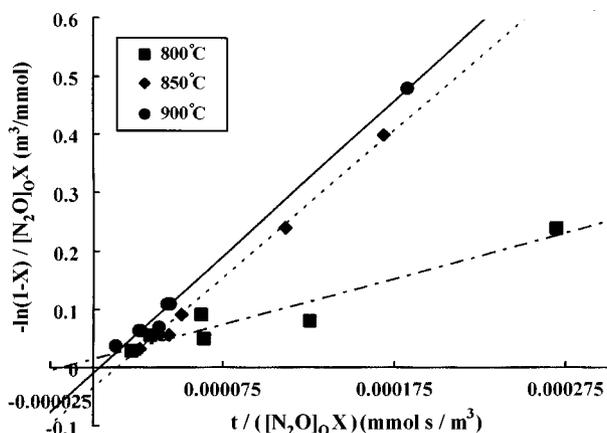


Fig. 6. Heterogeneous reaction rate of N_2O decomposition over CaO.

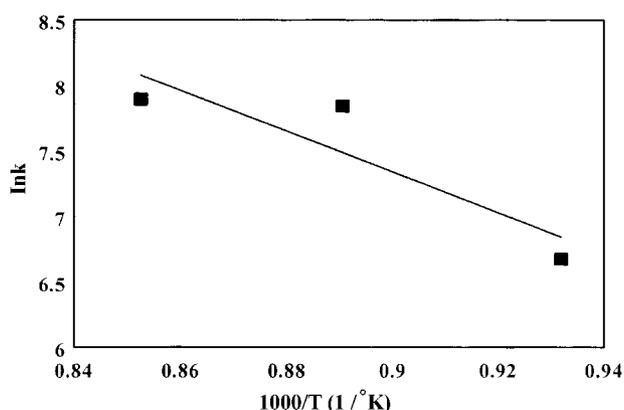


Fig. 7. Arrhenius diagram on N_2O decomposition over CaO.

concentration can be calculated by combining Eqs. (7) and (8).

In a typical reaction condition C_b (N_2O) is 1.58×10^{-6} mmol/ m^3 and calculated $C_b - C_a$ is 3.21×10^{-10} mmol/ m^3 at 850 °C, i.e., C_b is similar value to C_a . Therefore, intrinsic reaction rate can be calculated by using bulk concentration of N_2O . The results of experiments applied to theoretical equation are expressed in Fig. 6. Reaction rate constant (k'_s) of the reaction are 794, 2,541, 2,690 s^{-1} , respectively at 800, 850, 900 °C

Arrhenius plotting was done and expressed in Fig. 7 in order to obtain activation energy of the related reaction and frequent factor (A), and the obtained activation energy and frequent factor were 128.9 KJ/mol, 1.77×10^9 , respectively. N_2O decomposition rate equation on the surface of CaO including above two parameters is expressed as the following equation.

$$\frac{d[N_2O]}{dt} = \frac{1.77 \times 10^9 \exp[-128.9/(RT)] K_{N_2O} [N_2O]}{(1 + K_{N_2O} [N_2O])}$$

CONCLUSION

The conclusions of N_2O decomposition on the surface of calcium oxide are as follows:

1. Creation of NO in N_2O decomposition reaction was not detect-

able, and the most of the N_2O seemed to convert to N_2 . Also, as the temperature increased, the conversion of the reaction increased.

2. When CO_2 coexisted with N_2O and the concentration of CO_2 was over 10%, catalytic decomposition of N_2O decreased by reverse calcination of limestone by CO_2 . When CO coexisted with N_2O , N_2O decomposition reaction was promoted.

3. Reaction rate equation of N_2O decomposition by using CaO catalyst is as follows:

$$\frac{d[N_2O]}{dt} = \frac{1.77 \times 10^9 \exp[-128.9/(RT)] K_{N_2O} [N_2O]}{(1 + K_{N_2O} [N_2O])}$$

4. CaO made of domestic limestone showed a catalytic activity to N_2O decomposition.

NOMENCLATURE

r	: reaction rate [mol/ m^3 s]
K	: equilibrium constant [-]
k'_s	: reaction rate constant [1/s]
s	: active sites in the surface of CaO [-]
τ	: residence time [s]
F	: flow rate [m^3 /s]
T	: temperature [K]
W	: packed weight of CaO [kg]
$[i]_0$: initial concentration of i component [mol/ m^3]
ρ	: density of CaO particle [kg/ m^3]
X_i	: conversion of i component [-]
k_m	: reaction rate constant [mol/ m^3 s]
G	: mass velocity [kg/ m^2 s]
a_m	: external surface area/unit mass of particle [m^2 /kg]
a_t	: total external area of a particle [m^2 /kg]
D	: bulk diffusivity [m^2 /s]
C_b	: bulk concentration [mmol/ m^3]
C_a	: surface concentration [mmol/ m^3]
dp	: particle diameter [m]

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