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A Study of Nitrous Oxide Decomposition over Calcium Oxide in Combustion Condition

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Abstract−A study of N_2O decomposition reaction over a bed of CaO particles in a fixed bed reactor has been conducted. Effects of parameters such as concentration of inlet N_2O, reaction temperature and effects of CO, CO_2, O_2, and NO gas presented in the combustion gas environment have been investigated. The experiment showed that the N_2O decomposition reaction was accelerated by the increase of reaction temperature, and the existence of CO, while the reaction was hindered by the existence of CO_2, NO. O_2 also affected the N_2O decomposition. Heterogeneous gas-solid reaction kinetics were proposed for the reaction conditions and compared with homogeneous reaction kinetics.

Key words : Nitrous Oxide Decomposition, Calcium Oxide, Kinetics

INTRODUCTION

The emission of N_2O has been recognized as one of the major causes of global warming and harmful effect on the ozone layer in the upper atmosphere. The N_2O, which is emitted to the environment mostly during natural processes, has been reported to have over 200 times stronger greenhouse effect than CO_2. Major source of N_2O generation is the oxidation of N_2 component by bacteria in the soil, destruction of the forests and land clearing, and excessive utilization of nitrogenous fertilizers. Also, the incineration of wastes and the power generation using fossil fuel can be another source [de Soete, 1994]. Around 10% of N_2O release is reported to be contributed by coal combustion process.

The circulating fluidized bed (CFB) boilers have been welcomed in utility and waste incineration business for their excellent combustion and boiler efficiency. However, the fluidized bed combustor is reported to release significantly higher amount of N_2O than other types of coal burning combustors [Åmand and Andersson, 1989]. There were a few suggestions for reduction or destruction of N_2O leaving CFB combustor such as by increasing the combustor temperature [Suzuki et al., 1996], but the method is difficult to apply since keeping the inside combustor temperature above 950 °C may cause damage in the boiler parts and increase the opportunities for clinker formation.

For the CFB combustors limestone ($CaCO_3$) is usually injected with feed coal for sulfur removal and the limestone also decompose N_2O over unused CaO. Thus the emission is suppressed by the existence of CaO [Chang et al., 2000; Johnson and Jensen, 1994; Peter et al., 1993]. There are gas-solid reactions on the surface of CaO with N_2O, and the reaction order is suggested to be first order [Shimizu et al., 1993]. In this study the decomposition of N_2O over CaO with various combustion gas components, which simulates the gas composition of lower parts of CFB combustor, was conducted. The effects of reacting temperature and content of CO_2, CO, NO, and O_2 on N_2O decomposition were analyzed, and a kinetic study considering the catalytic effect of CaO was conducted [Klvana et al., 2002; Panczyk and Rzinski, 2004].

The kinetic approach of N_2O decomposition over calcium oxide has been suggested by many authors on either case of fluidized bed combustion [Johnsson et al., 1997; Satsuma et al., 2000; Simizu et al., 1993] or fixed bed combustion [Satsuma et al., 2000]. However due to the complex nature of N_2O decomposition mechanism, most efforts were concentrated on the generalization on overall kinetics. In order to understand the fundamental role of each constituent in the combustion environment, this work concentrated on the role of major combustion products on N_2O decomposition mechanism.

THEORETICAL APPRAOCH

In this work, a set of heterogeneous reaction mechanisms using the Langmuir & Hinshelwood model [Smiths, 1981] was suggested and it is as follows:

$$N_2O + s \xrightarrow{K1} N_2Os \quad (1)$$

$$N_2Os \xrightarrow{ks1} N_2 + 1/2O_2 + s \quad (2)$$

The mechanism (1) is adsorption of N_2O on CaO surface. The s is an active site on the surface of CaO where N_2O adsorption and decomposition can occur, and N_2Os describes the adsorbed state of N_2O on the active site of CaO. If Eq. (2) is the rate determining step which means the slowest reaction, equation of reaction can be expressed as follows:

$$r = \frac{k_{s1}K_1S[N_2O]}{1+K_1[N_2O]} = \frac{k'_{s1}K_1[N_2O]}{1+K_1[N_2O]} \quad (3)$$

Where $k'_{s1}=k_{s1}S$ and S is the number of total active sites on CaO.

In general, CFBC utilizes the technique of sub-stoichiometric oxygen supply ratio in the lower part of CFBC to control NO_x emission, CO concentration in this area is usually high [Basu and Fraser, 1991]. CO also can be adsorbed on CaO and it affects the N_2O decomposition. A bimolecular reaction mechanism is suggested in this work. The heterogeneous mechanism involving the reaction between

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CO and N_2O on CaO surface is as follows:

$$CO + s \xrightarrow{K2} COs \quad (4)$$

$$N_2Os + COs \xrightarrow{ks2} N_2 + CO_2 + 2s \quad (5)$$

When CO coexists with N_2O then Eq. (5) as well as (2) can be considered for the N_2O decomposition mechanism. The decomposition reaction rate can be increased with CO. If the mechanism (5) is considered to be the rate determining step and we do not differentiate the N_2O adsorption site and CO adsorption site, we can suggest following rate equation:

$$r = \frac{k_{s2}SK_1[N_2O]K_2[CO]}{(1+K_1[N_2O]+K_2[CO])^2} = \frac{k'_{s2}K_1[N_2O]_o^2(1-x)(\alpha-x)}{(1+K_1[N_2O]_o(1-x)+K_2[N_2O]_o(\alpha-x))^2} \quad (6)$$

Where, x is the conversion of $[N_2O]$, $\alpha=[CO]_o/[N_2O]_o$, and $k'_{s2}=k_{s2}S$.

After the arrangement we get:

$$A^2\ln\frac{\alpha-x}{\alpha(1-x)} - 2AB[N_2O]_o\ln\frac{(\alpha-x)^\alpha}{\alpha^\alpha(1-x)} = -k'_{s2}\tau(\alpha-1)[N_2O]_o \quad (7)$$

Where, $[N_2O]_o$ is the concentration of introducing N_2O, $A=1+(K_1+K_2\alpha)[N_2O]_o$, $B=K_1+K_2$, and the residence time(t) is $\tau=W/\rho F$. Where W is mass of CaO bed, ρ is the particle density, F is flow rate of gas.

The homogeneous mechanism in this case will be as follows:

$$N_2O + CO \xrightarrow{k3} N_2 + CO_2 \quad (8)$$

The reaction rate will be described as follows:

$$r=k_3[N_2O][CO] \quad (9)$$

CO_2 is considered to hinder the N_2O decomposition. CO_2 adsorbs on the CaO surface and blocks N_2O adsorption. CO_2 and N_2O compete with active site on CaO. But CO_2 does not seem to participate in the N_2O decomposition reaction. With (1), (10), and (11), the mechanism becomes as follows:

$$CO_2 + s \xrightarrow{K3} CO_2s \quad (10)$$

$$N_2Os + CO_2s \xrightarrow{ks3} N_2 + 1/2O_2 + CO_2s + s \quad (11)$$

$$r = \frac{k_{s3}S[N_2O]}{1+K_1[N_2O]+K_3[K_2CO_2]} \quad (12)$$

EXPERIMENTAL

The experimental apparatus used in this study, which is shown in Fig. 1, consists of a reactor, sets of flow meters, a pre-heater, and a set of gas analyzer. The reactor was made of quartz tube with inside diameter of 2.5 cm and height of 50 cm. The middle part of the inside of the reactor is installed with a sintered quartz plate to support the CaO particles. The gas flow is vertically downward through the reactor toward the sintered plate. In order to heat the reactor, an infrared furnace with a PID controller is used. A flow meter was installed at the upstream of gas input in order to regulate gas flow. The reactant gas was pre-heated while passing the inlet tube with a heating band before introduced to the reactor.

Mixtures of CaO particles (0.4 g) and quartz beads (4 g) were loaded on the sintered quartz plate inside the reactor. Nitrogen gas

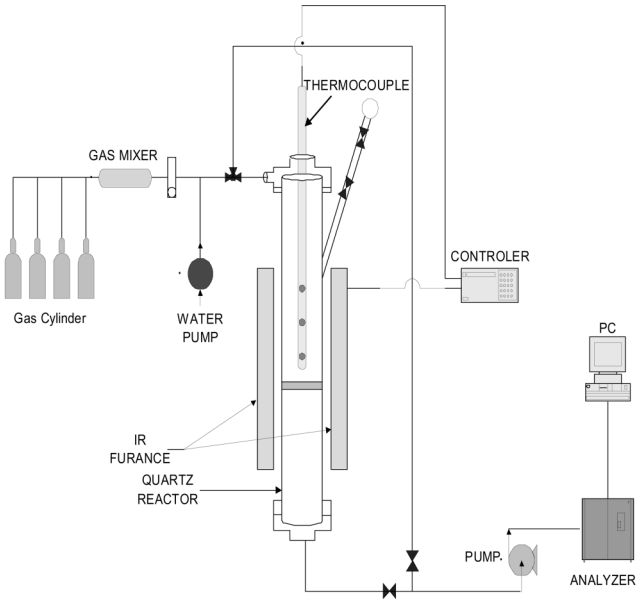

Fig. 1. Diagram of the experimental apparatus.

Table 1. Experimental conditions

Variables	Experimental conditions
Bed materials	CaO (0.4 g)+quartz (4 g)
Flow rate (*l*/min)	3.5
Temperature (°C)	800-900
N_2O (ppm)	200-1,000
CO (ppm)	50-3,000
CO_2 (%)	3-20

was introduced into the reactor during the heating of the reactor. When the temperature and other conditions of the reactor reached the preset experimental condition, the reactant gas was introduced into the reactor. The calcium oxide (CaO 54.14%, MgO 0.94%, H_2O 0.02%) used in the experiment was prepared from the limestone in Chechun province in Korea. It was prepared by calcining at 1,123 K in reactor for 2 hours in N_2 environment. The experimental conditions are listed in Table 1.

RESULTS AND DISCUSSION

In this study the governing reaction was assumed to be the intrinsic reaction. Therefore, we had to estimate the difference between surface and bulk concentration of N_2O over CaO particle. When the concentration difference is acceptably small, we can consider that the mass transfer between the bulk and the surface does not affect the total kinetics. The difference between the bulk concentration and the surface concentration can be simply correlated in terms of dimensionless group, i.e., in terms of j-factor [Smith, 1981]. The j-factor for mass transfer is the function of Sherwood number, $k_m\rho/G$, the Reynolds number d_pG/ρ, and Schmidt number $\mu/\rho D$. The equation is as follows [Shun et al., 2001];

$$j_D = \frac{k_m\rho}{G}\frac{a_m}{a_t}\left(\frac{\mu}{\rho D}\right)^{2/3} \quad (11)$$

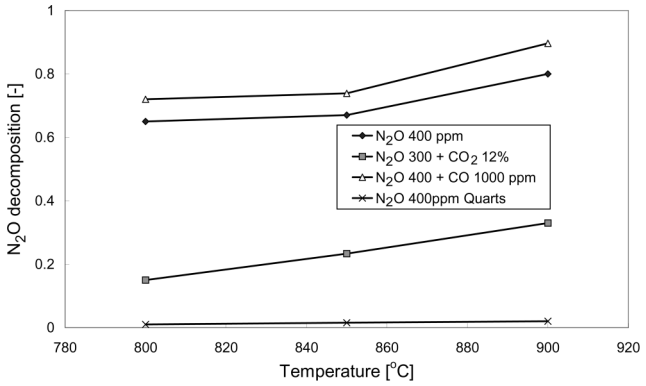

Fig. 2. The effects of temperature on N_2O decomposition with various reactants.

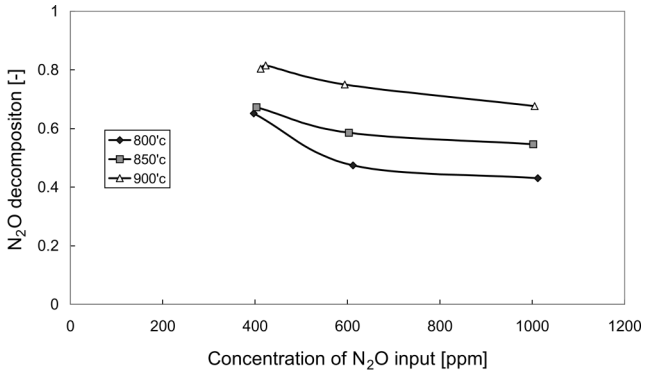

Fig. 3. The effect of concentration on N_2O decomposition.

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

$$r_p = k_m a_m (C_b - C_a) \quad (12)$$

The difference between the bulk concentration and the surface concentration can be calculated by combining Eqs. (11) and (12). In a typical reaction condition C_b (N_2O) is 1.6×10^{-6} mmol/m^3 and calculated $C_b - C_a$ is 3.2×10^{-10} mmol/m^3 at 850 °C. Since the concentration C_b is similar to C_a, intrinsic reaction rate can be calculated by using the bulk concentration of N_2O. The external diffusion resistance is negligible and the kinetics of N_2O decomposition is mainly the intrinsic kinetics.

Fig. 2 presents the effects of temperature on N_2O (400 ppm) decomposition in N_2 environment, N_2O (300 ppm) with CO (1,000 ppm) decomposition and N_2O (400 ppm) with 12% CO_2 decomposition, respectively. The thermal effect on N_2O decomposition was also compared by installing quartz sand instead of CaO/quartz sand mixture. The thermal effect on N_2O decomposition was negligible. The decomposition of N_2O increased over CaO bed with the increase of the temperature. The existence of CO further enhanced the N_2O decomposition, whereas CO_2 hindered the N_2O decomposition over CaO. Table 2 listed the surface area before and after the reaction. The surface area of CaO did not vary by decomposition of N_2O in N_2 environment only, but the area was significantly reduced in N_2 and CO_2 environment. Thus CO_2 hinders the N_2O decomposition reaction by adsorption of CO_2 on CaO surface.

Fig. 3 presents the effect of feed concentration of N_2O on its decomposition. The decomposition decreased with the increase of the N_2O concentration due to the relative decrease of the active site on CaO surface. A heterogeneous reaction mechanism was proposed and the mechanism as explained in Eqs. (1), (2), (3) showed best fit. The detailed result was reported in the previous paper [Shun et al., 2001].

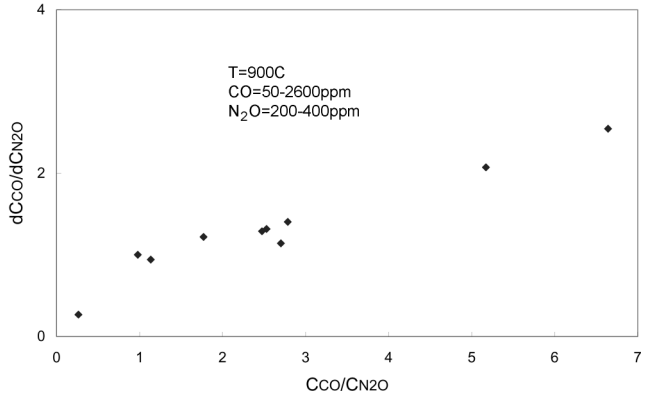

Fig. 4. The effect of feed CO/N_2O ratio on the decomposition ratio of CO/N_2O.

Fig. 4 presents the effect of initial CO/N_2O ratio on the ratio of CO/N_2O decomposition. The decomposed mole ratio of CO/N_2O was almost equal during those of feed CO/N_2O varying from 1 to 3. That implies when CO exists the mechanism of the decomposition of N_2O prefers bi-molecular reaction, and the reaction mechanism of (4) and (5) was proposed. However, further increase of feed CO/N_2O ratio increased the ratio of decomposition further, and more CO is consumed than N_2O is decomposed. This violates the 1 to 1 ratio of the reaction between N_2O and CO. It may due to the adsorption of CO to CaO surface [Shun et al., 2001]. The Fig. 5 and the Fig. 6 compares the heterogeneous mechanism of CO and N_2O decomposition as was shown in heterogeneous Eq. (6) and (7) and a homogeneous mechanism (8). Even though the correlation coefficient is low, the heterogeneous model shows the better fit. It seems the simultaneous reaction mechanisms (2) and (5) are competing with each other, and also CO is adsorbed on CaO surface for N_2O decomposition with the existence of CO.

Table 2. $CaCO_3$ and CaO analyses

Limestone		CaO, 54.14%; MgO, 0.94%; H_2O, 0.02%
BET surface area [m^2/g]	Limestone	4.36-4.52
	CaO	7.52-8.02
	After N_2O decomposition (N_2 only)	7.32-7.94
	After N_2O decomposition (N_2, 80%, CO_2 20%)	2.35

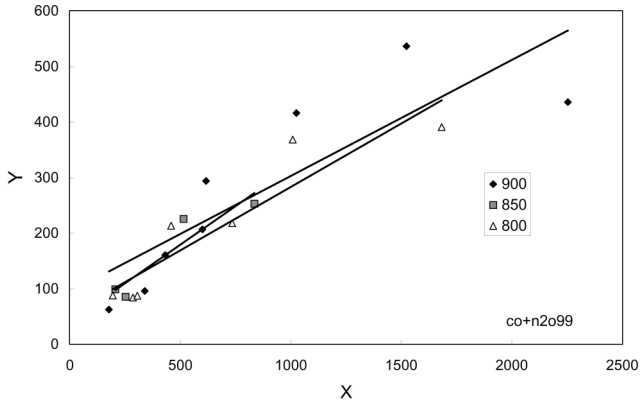

Fig. 5. The heterogeneous mechanism CO and N_2O decomposition.

$$X = AB[N_2O]_o \ln\frac{(\alpha - x)^{\alpha}}{\alpha^{\alpha}(1-x)} \quad Y = A^2 \ln\frac{(\alpha - x)}{\alpha(1-x)}$$

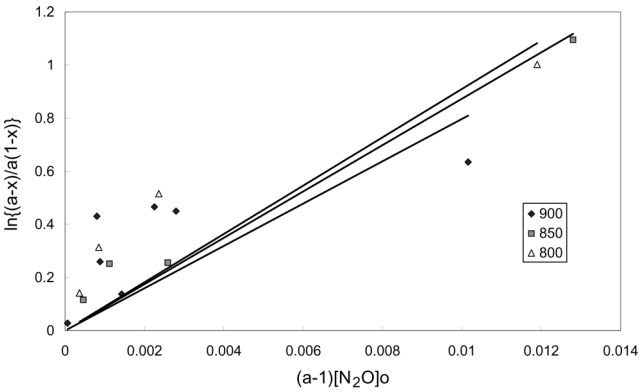

Fig. 6. The homogeneous mechanism of CO and N_2O decomposition.

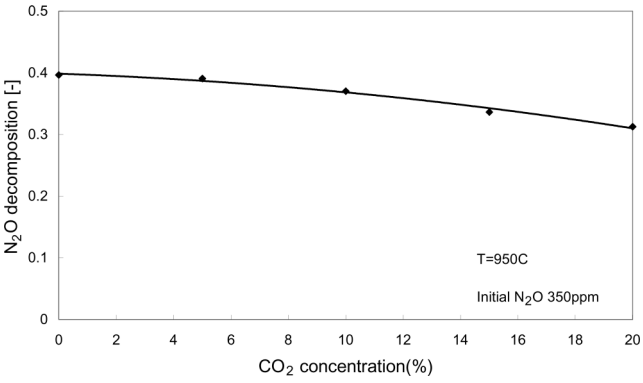

Fig. 7. The effect of CO_2 concentration on N_2O decomposition.

The influence of CO_2 on N_2O decomposition over CaO is presented in Fig. 7. As the concentration of CO_2 increased, the N_2O conversion was gradually decreased until the concentration of CO_2 reached 20%. The variation of N_2O decomposition was about 10% from 0% to 20% of CO_2. CO_2 and N_2O seemed to compete with each other over the active site on CaO, and which resulted in the hindrance of catalyst decomposition of N_2O on the CaO surface [Chang et al., 2000].

Fig. 8 presents the effect of the initial concentration of N_2O and

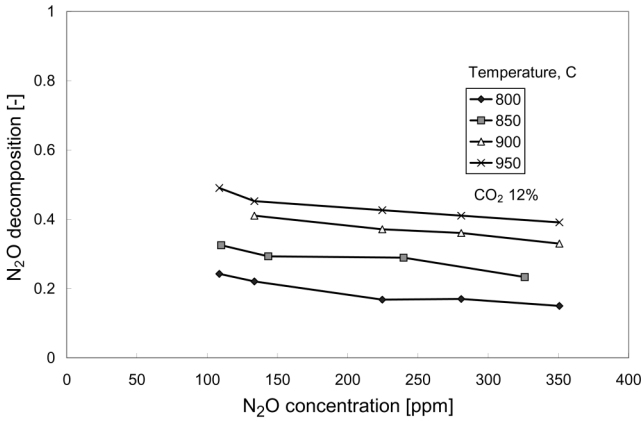

Fig. 8. The effect of feed N_2O concentration and temperature on its decomposition with CO_2.

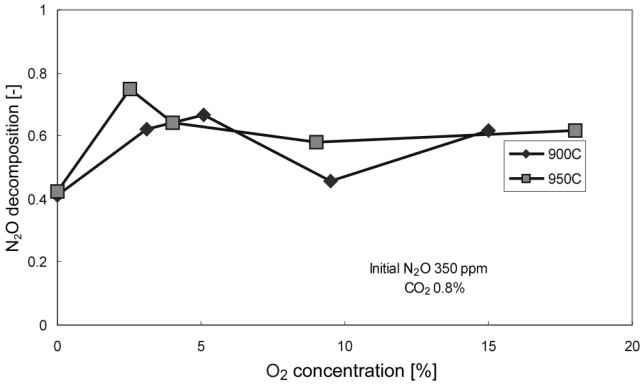

Fig. 9. The effect of O_2 on N_2O decomposition.

reaction temperature on N_2O decomposition when the concentration of CO_2 was fixed at 12%. The conversion decreased gradually with the increase of the concentration due to the relative decrease of the CaO surface. However, the conversion increased with the temperature. That implies the reaction of CO_2 adsorption on the CaO is occurring in the reaction condition, but it decomposes with the increase of the temperature. There is no evidence of direct involvement of CO_2 on N_2O decomposition, but it still hinders the decomposition. It is concluded that CO_2 competes with the N_2O on active sites on CaO. Thus, the reaction mechanisms of (10), (11), and (12) were proposed.

The Fig. 9 shows the effect of O_2, and O_2 also affected N_2O decomposition. The decomposition increased until O_2 was 2.5-4% and also with the increase of the temperature [Satsuma et al., 2000]. Above the concentration the decomposition rate stabled. With limited information, it seems that O_2 refreshes the CaO surface, but further increase of O_2 partial pressure does not affect either N_2O adsorption or clearing the CaO surface.

NO also showed the hindering effect in N_2O decomposition. The effect was, however, relatively low. Fig. 10 shows the effect of NO concentration on N_2O decomposition. The reaction was monitored with the CO of 10% and 20% concentrations.

In general operation of CFBC, CaO is introduced in the lower part of the combustor. The addition of CaO in the lower part of the combustor will decrease N_2O formation; however, it increases NO

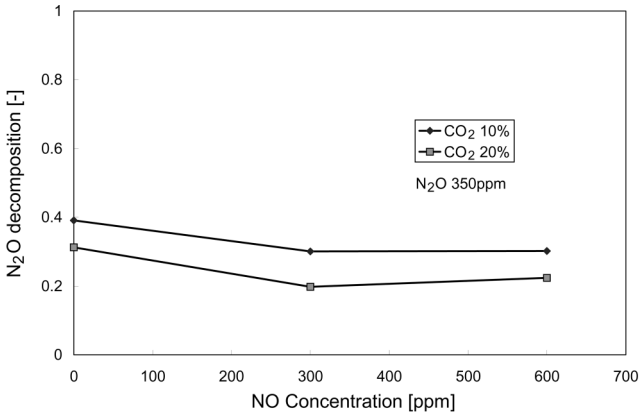

Fig. 10. The effect of NO concentration on N_2O decomposition.

emission [Shimizu, 2000]. In order to accomplish the simultaneous reduction of both NO and N_2O in commercial CFB boilers, the supply of limestone which can reduce N_2O at the lower part of the combustor will be a measure for N_2O control; that and typical SNCR (selective non catalytic reaction) techniques can be applied at the flue gas stage [Ljungdahl, 2001] to remove NO with increased with the injection of limestone.

CONCLUSION

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

1. CaO from domestic limestone showed catalytic activity on N_2O decomposition.
2. A set of heterogeneous mechanisms of N_2O decomposition with CO and CO_2 were proposed from the experimental data.
3. CO promoted N_2O decomposition.
4. CO_2 hindered N_2O decomposition and the increased CO_2 concentration gradually decreased N_2O decomposition.
5. O_2 increased N_2O decomposition up to 3%; then above the concentration the effect was not clear.
6. NO also hindered N_2O decomposition.
7. In order to reduce N_2O and NO simultaneously in the CFBC combustor, feeding of CaO in the lower part of the combustor is recommended. The increased NO should be removed from flue gas by SNCR method.

NOMENCLATURES

r : reaction rate
K : equilibrium constant
k_s' : reaction rate constant [1/s]
S : total active sites existing in the surface of CaO
F : flow rate [m^3/s]
X_i : conversion of i component
T : temperature [K]
W : packed weight of CaO [kg]
$[i]_o$: initial concentration of i component
α : ratio of CO and N_2O concentration
ρ : density of CaO particle [kg/m^3]
τ : residence time [s]
μ : gas viscosity [kg/m-s]
D : molecular diffusivity [m^2/s]

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