CATALYTIC REDUCTION OF NITRIC OXIDE BY CARBON MONOXIDE OVER CALCINED LIMESTONE

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The rate of "NO" reduction by carbon monoxide over calcined limestone was measured over a temperature range (588–922°C) by use of a fixed bed flow reactor. The calcined limestone was found to have a high catalytic activity for "NO" reduction by carbon monoxide and the obtained rate exceeds the rate of catalytic as well as non-catalytic NO reduction by char. A significant effect of calcined lime on NO reduction by carbon monoxide within a calciner and a fluidized bed coal combustor is suggested.

Introduction

The oil shock has compelled us to again utilize coal as an alternative energy resource, mainly for power generation and cement production. The emission control of nitric oxide originating from fuel-bond nitrogen in coal poses a significant concern in our present environmental problems. The control of NO emission from a conventional pulverized fuel combustor and from a fluidized bed combustor has been extensively investigated.^{1,2,3,6,7)} Effective modifications of combustion have been developed to a point of commercial availability. Kinetic information about reactions which destroy NO_x are becoming available,^{4,5,10,11)} thus allowing the development of mathematical models which describe the behavior of NO emission from fluidized bed combustors.

The recent introduction of NSP (new suspension preheater) kiln systems,^{8,12)} originally developed to reduce energy consumption, was also found to contribute significantly to the reduction of NO_x emission.¹²⁾ However, the emission level of NO_x by the NSP kiln system is still unacceptably high compared with that achieved by both the conventional and fluidized bed combustors. Consequently, the development of a modified NSP kiln which can reduce NO_x emission has been carried out. However, the mechanism of NO_x destruction has not been fully investigated. The need to carry out this research is thus clearly defined. The purpose of the work reported in this paper is part of a large program to examine the possibilities of controlling NO_x emission from cement kilns. The importance of calcined lime in NO_x reduction has been pointed out.¹³⁾ However, the kinetic information has not been available. The objective of this part of the study is to investigate the catalytic effect of calcined limestone on NO reduction and to evaluate

the relative importance of NO_x reduction by calcined limestone and that by *in situ* formed char.^{4,5)}

1. Experiments

A schematic flow diagram of the experimental apparatus is shown in Fig. 1. A fixed bed reactor (a quartz tube 20 mm in ID, 1000 mm in height) was employed for the experiments. Iwato limestone ($d_p = 417$ microns), the analysis of which is given in Table 1, was weighed to an accuracy of 1 mg and mixed with quartz sand of similar size. The resulting mixture was packed into the quartz tube reactor to a predetermined height of 30 mm so that a significant conversion level of nitric oxide could be attained. Preliminary experiments confirmed that the reaction of NO reduction by carbon monoxide was not catalyzed by quartz sand. This fixed bed of diluted particles was located in the middle part of an electric furnace so that a constant temperature could be maintained within the reacting bed. The temperature was measured by a chromel-alumel thermocouple which was sheathed in a high-purity alumina tube.

Fig. 1. Schematic diagram of experimental apparatus. a, CO-Ar mixed gas cylinder; b, NO-Ar mixed gas cylinder; c, N₂-gas cylinder; d, mass flow controller; e, orifice meter; f, rotameter; g, mixer; h, four-way ball valve; i, sampling coil; j, manometer; k, stop valve; p, electric furnace; q, reactor; v, gasometer; w, thermocouples.

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Table 1. Analysis of limestones

	CaO	MgO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Weight loss after calcination
Iwato limestone	55.43	0.36	0.13		0.12	43.67
Buko limestone	54.8	0.6	0.5	0.2	0.1	43.0

Table 2. Scope of the experiment

Inlet concentration	NO	496–1860 ppm
	CO	1610–38500 ppm
Reaction temperature		861 K–1195 K 588–922°C
Residence time		1.47–22.4 ms
Inlet concentration, ratio of CO to NO (α)		1–65

Table 3. Typical mass balances and product compositions

Run	Temp. [K]	Residence time [ms]	$\frac{[\text{NO}]_{\text{in}}}{[\text{CO}]_{\text{in}}}$ [—]	$[\text{NO}]_{\text{in}}$ – $[\text{NO}]_{\text{out}}$ [ppm]	$[\text{CO}]_{\text{in}}$ – $[\text{CO}]_{\text{out}}$ [ppm]	$[\text{CO}_2]_{\text{out}}$ [ppm]	$[\text{N}_2]_{\text{out}}$ [ppm]
1	1195	3.17	5.16	1120	1260	1150	730
2	1054	3.81	10.2	1050	1490	1120	590
3	993	11.8	5.16	1190	1120	1200	820
4	965	4.63	6.44	440	420	460	270
5	905	13.1	5.10	810	830	720	460

The bed temperature was controlled by a conventional controller.

Before measuring the rate of NO reduction the bed temperature was increased to 900°C within two hours and maintained at this temperature for about 60–120 minutes until carbon dioxide formed by calcination of the limestone was not detected by gaschromatograph. Thus the temperature was set to a value predetermined for the experiment.

A carbon monoxide/argon mixture and a NO/argon mixture at constant pressure was supplied from respective gas cylinders fitted with flow and pressure regulating valves. The gas flow rate was controlled by a needle valve attached to a mass flow controller and metered by a rotameter or orifice flowmeter. A mixture of NO and carbon monoxide diluted by argon was then introduced into the reacting part of the reactor. The gaseous reaction products were intermittently withdrawn from the reactor and analyzed by a chemiluminescent NO_x analyzer and gas chromatographs. The scope of the experiment is shown in **Table 2**.

2. Experimental Results and Discussion

2.1 Reaction scheme

The initial series of experiments were carried out for a ratio of concentration of CO to that of NO at the inlet of $\alpha = 1.0$ –10.0 to investigate the material balance of the reaction. Typical results are shown in **Table 3**. The material balance observed indicates that the carbon dioxide formed by the reaction coincided approximately with both the amounts of consumed nitric oxide and carbon monoxide as

$$\begin{aligned} [\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} &= [\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}} \\ &= [\text{CO}_2]_{\text{out}} - [\text{CO}_2]_{\text{in}} \end{aligned} \quad (1)$$

where

$$[\text{CO}_2]_{\text{in}} = 0$$

From the material balance, the nitrogen formed by the reaction should be equal to Eq. (1). The observed amount of nitrogen formed was rather erratic due to leakage from the air. However, these results do not appear to be contradictory to the following reaction scheme:

which is catalyzed over the surface of calcined lime. Thus the reaction rate was analyzed by assuming the above reaction scheme.

2.2 Measurement of rate

The rate was evaluated by assuming that the surface-catalyzed reaction was first-order with respect to both nitric oxide and carbon monoxide as

$$r = k[\text{NO}][\text{CO}] \quad (3)$$

The material balance for reaction component for a differential slab of the tubular reactor is given as

$$Fdc = (-r)dV \quad (4)$$

Introducing α , the ratio of the concentration of carbon monoxide to that of nitric oxide at the inlet of the reactor, and x , the extent of the reaction of NO, Eq. (3) results in

$$r = kC_0(1-x)C_0(\alpha-x) \quad (5)$$

Equation (4) integrated by using Eq. (5) results in

$$\ln \frac{\alpha-x}{\alpha(1-x)} = k(\alpha-1)C_0t \quad (6)$$

where t , the residence time, is defined as $t = V/F$.

The experiment can be carried out by measuring the left-hand side at various t and α . As shown in **Fig. 2**, the left-hand side of Eq. (6) was linearly pro-

Fig. 2. Second-order reaction verified by straight lines.

Fig. 3. Arrhenius plots based on second-order kinetics.

portional to the term $(\alpha - 1)C_0t$ on the right-hand side of Eq. (6). This fact appears to justify the above assumption concerning the kinetics expressed by Eq. (3). The rate constant was measured from the inclination of the straight line in Fig. 2 by use of the least squares method. The Arrhenius plots obtained thus are indicated in Fig. 3. The activation energies and frequency factors obtained from Fig. 3 are summarized in Table 4.

Our previous investigation concerning the reduction of NO emission from a fluidized-bed combustor demonstrated that char provided a catalytic surface for NO reduction by carbon monoxide.⁵⁾ To evaluate the relative importance of catalytic activity of char as well as calcined limestone, the rate of NO reduction over calcined lime was compared with our previously obtained rate of the char-catalyzed reaction where the rate was assumed to be first-order with respect to NO. This can be justified by choosing a significantly large value of α , namely by keeping the concentration of CO constant within the reactor. Thus the equation is expressed as

Table 4. Reaction rate constant

Temp. range [K]	Reaction rate constant [ppm ⁻¹ ·s ⁻¹]	Activation energy [kJ·mol ⁻¹]
858–943	$3.41 \times 10^7 \exp\left(-\frac{2.11 \times 10^4}{T}\right)$	1.75×10^2
943–1195	$1.56 \times 10^2 \exp\left(-\frac{8.92 \times 10^3}{T}\right)$	7.42×10^1

$$r = k'[\text{NO}] = C_0(1 - x) \quad (7)$$

By introducing Eq. (7) into Eq. (4) and integrating, we obtain

$$-\ln(1 - x) = k't \quad (8)$$

The experiment is carried out by measuring the left-hand side of Eq. (8) at various t . Since the experimental results indicated that $-\ln(1 - x)$ is linearly proportional to t , k' is evaluated from the inclination. The results are shown in Fig. 4, where α was chosen on the basis of the concentration profiles of NO and CO within the typical calciner reported elsewhere.¹²⁾ The inlet concentrations of NO and carbon monoxide were respectively 650 ppm and 37000 ppm.

2.3 Considerations concerning experimental conditions

The effect of mass transfer resistance through the film of the calcined lime particle was estimated as follows. As shown in Fig. 3, the activation energy is reduced over a range of temperatures higher than 943 K. Thus the maximum rate attainable in the absence of mass transfer resistance was assumed to be $k = 0.426$ [ppm⁻¹, s⁻¹], which was obtained by extrapolating the rate in the temperature range of 858–943 K in Fig. 3. The rate constant of a first-order reaction with respect to NO concentration was obtained by multiplying the inlet concentration of carbon monoxide (5000 ppm). The film resistance of mass transport, which was evaluated by use of the Yagi and Wakao equation,¹⁴⁾ was less than 9% of the rate evaluated by the above assumption. Thus it was considered justified to neglect the effect of mass transport resistance.

The effects of intraparticle mass transport on the decreased activation energy (over 943 K) was also evaluated by assuming that the particles are spherical. The results are shown in Table 5, where the diffusivity was estimated by Fujita's equation. The effective diffusivity was calculated by assuming that the ratio of void fraction of particles to the tortuosity factor was equal to 0.25. The reaction rate also estimated by extrapolating the rate corresponding to the temperature range (858 K–943 K) was employed. This assumed rate was significantly higher than the rate experimentally obtained. Thus the effectiveness was

Fig. 4. Rate catalysed by calcined limestone compared with rate of catalytic NO reduction over char surface as well as rate of non-catalytic NO reduction.

Table 5. Evaluation of effectiveness factor

Temperature [K]	1173	1073	973	873
Rate constant [s ⁻¹]	2130	492	68.0	5.45
$\mathcal{D}_{\text{NO-Ar}}$ [cm ² ·s ⁻¹]	2.81	2.39	2.00	1.64
$\mathcal{D}_e$ [cm ² ·s ⁻¹]	0.468	0.398	0.333	0.273
ϕ [—]	1.41	0.733	0.298	0.0932
Effectiveness factor: η [—]	0.889	0.966	0.994	0.999

considered to be much closer to unity than those indicated in Table 5, and the intraparticle resistance is considered to be insignificant over the temperature range employed for the present investigations.

In this analysis, the flow within the bed was assumed to be plug flow since the height of the fixed bed employed in this study was approximately 50 times larger than the diameter of the packing materials consisting of inert quartz sand and calcined lime of a similar size.⁹⁾ Effects of non-uniform temperature distribution due to the heat of reaction may be neglected because the maximum concentration of NO was extremely low (1860 ppm).

2.4 Discussions

The results together with the kinetic data obtained for the catalytic NO reduction by carbon monoxide over char surface and the noncatalytic NO reduction by char are shown in Fig. 4.^{4,5)} It should be noted that the ratio of carbon monoxide concentration to NO concentration employed for char-NO-CO reaction system is approximately equal to the ratio employed for lime-NO-CO reaction system. Under those conditions the rate constants of the two systems were of the same magnitude. This indicated that the catalytic activity of both is comparable. However, the

relative importance of these two catalytic surfaces for "NO_x" reduction within the fluidized-bed combustor does not depend only on the catalytic activity of these surfaces, but also on the available surface areas, which is controlled by the concentrations of both of the char and limestones and the extent of calcination and sulfur retention of the limestone. Thus an extensive investigation must be carried out to elucidate their relative importance for NO_x reduction. Furthermore, NO can be reduced by noncatalytic heterogeneous reaction with char and this rate was increased or decreased by the coexisting oxygen depending on the temperature.^{10,11)}

The observed activation energy of NO reduction by carbon monoxide over calcined lime was decreased over the temperature range (720–922°C). This phenomena will be observed if two successive reactions participate in NO_x reduction. No change of product distribution above this point has yet been observed and the existence of an intermediate product cannot be detected.

To confirm the catalytic activity of calcined limestone, the same experiment was carried out by the use of a different limestone, Buko, the analysis of which is also shown in Table 1. The results obtained can be compared with the data for Iwato limestone, in Fig. 3.

In spite of the different content of impurities, the rate for Buko limestone coincided with the previous data within the range of experimental error over a temperature range of practical importance. This indicates the catalytic activity is not limited to Iwato limestone and the catalytic effects of calcined lime on NO reduction by carbon monoxide cannot be attributed to any special component of impurity contained in Iwato limestone.

Conclusion

A kinetic study concerning NO reduction by carbon monoxide catalyzed over a calcined lime surface was carried out. The calcined lime was found to have a high catalytic activity for NO reduction which can be compared with catalytic activities on *in situ* formed char. The rate constants were determined.

Nomenclature

C	= concentration of NO	[ppm]
C_0	= inlet concentration of NO	[ppm]
E_{act}	= activation energy	[kJ·mol ⁻¹]
F	= gas flow rate	[cm ³ ·s ⁻¹]
V	= volume of catalyst	[cm ³]
$[A]$	= concentration of A	[ppm]
$\Delta[A]$	= concentration of A produced by reaction	[ppm]
k	= second-order reaction rate constant	[ppm ⁻¹ ·s ⁻¹]
k'	= first-order reaction rate constant	[s ⁻¹]
r	= reaction rate	[ppm·s ⁻¹]
t	= residence time	[ms]
x	= conversion of NO	[—]
α	= inlet concentration ratio of CO to NO	[—]

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A NEW DECONVOLUTION TECHNIQUE IN BATCH ISOTOPE SEPARATION BY LASERS

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A new procedure has been proposed to investigate the effect of irradiation geometry and extract unbiased data from focused beam experiments in laser-induced photolysis and isotope separation. The model proposed here is shown to be advantageous over previous models experimentally and theoretically. The accuracy of this model was verified by comparing the parallel beam results and deconvoluted focused beam results using photolysis of CF_3Cl with O_2 added.

As a second step, the effectiveness of this method was tested for a binary system ($\text{CTF}_3/\text{CHF}_3$). By comparing the results with lenses of different focal length, the effect of focusing on selectivity was mathematically well described for two extreme cases: (1) tight focusing sufficient to produce cores with complete dissociation by one pulse near the focal spot for CTF_3 and CHF_3 , and (2) mild focusing without such cores. The advantage of performing the experiments with tightly-focused beam geometry before deconvolution experiments was also shown.

Introduction

The use of isotopically selective dissociation reactions induced by infrared laser beam is currently under investigation for such practical application goals as separation of ^{235}U , ^{13}C , ^2H (deuterium) and ^3H (tritium). For the development of this new technique, the following steps will be necessary. First, the most suitable working substance must be selected. Secondly, in batch experiments, reaction kinetics must be fully studied to obtain the best performance for the chosen working substance. In this step, such controllable variables as irradiation

wavelength, laser pulse duration, buffer gas pressure, gas temperature and pulse energy must be chosen to optimize the objective functions such as selectivity, operating pressure and reaction rate. At the same time, a study of a novel continuous reactor will be necessary for large-scale production. The continuous reactor should be so designed as to minimize deterioration of batch performance due to reflectivity loss, beam fluence inhomogeneity, back mixing, wall-catalyzed reaction and so on. Although the state of progress may vary from one isotope to another, the search for the optimal working substances is converging to a few substances, and most efforts are currently concentrated on the second step: optimization of reaction performance.

For ^{13}C separation, selectivity exceeding 60 at 13

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