Development of a Catalytic Two-Stage Combustion System

A new NOx-free combustion system using a new catalyst produced from stainless steel by special treatment was proposed and studied. A series of experiments verified that this new system could produce a high reduction rate of NO under the hostile flue gas conditions of a practical combustion process.

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SCOPE

Various kinds of NOx control techniques have been developed in the past ten years. However, it is still difficult to get NOx reduction rates higher than 80% only by the modification of the combustion system. On the other hand, the content of nitrogen-containing compounds in the fuel will tend to increase in the future as the need for burning low quality fuel will be increased. Therefore, further development of NOx control techniques in the combustion process of high-nitrogen-containing fuels such as residual oil or coal liquefied oil is still required. In this study a new NOx-free combustion system, called a catalytic two-stage combustion, was proposed and tested. The new catalyst, made from stainless steel invented and developed at our laboratory, was incorporated in the primary stage of this two-stage combustion system.

This system has the following advantages:

1) One need not introduce reducing species such as CO and H_2 since these species are generated in the primary stage of combustion.

2) The complete combustion of unburnt products generated in the primary stage is possible without catalyst because high temperature would still be maintained at the secondary combustion zone.

3) The cost of the catalyst is cheap compared to other precious metal catalysts such as platinum or palladium.

4) The space velocity of this catalytic system is at least 10 times as high as that of the conventional selective catalytic reduction processes.

CONCLUSIONS AND SIGNIFICANCE

The performance and reaction mechanism of a newly invented catalyst for the reduction of NO was studied by using a flow type reactor for the preliminary experiment and a model furnace with flue system in the practical stage. The first experiment showed that this new catalyst had the following remarkable characteristics:

1) The contact time required for the reduction of 90% NO is only 10 to 20 msec, which corresponds to $SV = 3.6 \times 10^5\ h^{-1}$ to $1.8 \times 10^5\ h^{-1}$ when the honeycomb type catalyst of 4 mm I.D. is used.

2) The conversion from NO to NH_3 at the catalyst layer was under 10% at 900°C.

The second part of the experiment gave the following important information for practical use:

1) The new catalyst works well even in the flue gases of heavy oil combustion, containing SOx and soot.

2) The final level of NO can be decreased to 48 ppm at a primary air ratio of 0.9.

Consequently, a series of experiments showed that this catalytic two-stage combustion was applicable to the industrial combustion process of high nitrogen fuels, effecting a high reduction rate of NO of up to 90% under the practical flue gas condition.

INTRODUCTION

Many sophisticated combustion technologies aiming at the control of NOx emission from the stationary combustion processes have been developed in recent years. For example, a two-stage combustion system consisting of a primary fuel-rich combustion and a secondary fuel-lean combustion makes it possible to reduce NOx emission to under 100 ppm for the combustion of low nitrogen

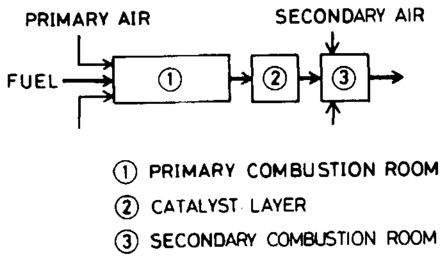

Figure 1. Basic outline of NOx-free combustion system.

gas or oil fuel. However, there is as yet no method of controlling NOx from the combustion of high nitrogen fuels such as residual or coal liquefied oils. A low quality fuel including a high nitrogen compound would have to be used more broadly for combustion in the future. Therefore, it is important to develop a new combustion system with levels of NOx emission under, say 50 ppm, even in the case of high nitrogen fuels.

In this study a new combustion system in which a new catalyst made from stainless steel (a stainless catalyst) is used to promote the reduction of NO in a two-stage combustion was proposed and tested. The outline of this system is shown in Figure 1. First, the emission of NO can be controlled in the fuel-rich combustion at the primary combustion room 1, then the residual NO can be reduced on the following stainless catalyst layer. Finally, unburnt species such as CO and H_2 generated at the primary stage are burnt in the secondary combustion room by the injection of a high speed tertiary air. The success of the system depends on whether the stainless steel catalyst can have a long life in the high temperature, hostile environment of the flue gas, which includes SOx and soot.

The following is an outline of this study. At first, the catalytic effect of the specially treated stainless steel on the reduction of NO in the reduced flue gas was investigated by using an electrically heated flow type reactor. The effect of the catalytic temperature and hydrogen concentration in the flue gas on the reduction of NO was investigated. Next, the gas-catalyst contact time required for the reduction of NO and the final products of NO conversion were examined. The reduction mechanism of NO on the stainless steel catalyst was then studied experimentally. Following the basic study, experiments using a medium size two-stage combustion furnace equipped with the stainless steel honeycomb catalyst were carried out. The corrosion effect of SOx and the blocking effect of soot were also examined to determine whether the new catalyst worked well even in the dirty environment of the actual flue gas. Finally, a demonstration experiment was carried out to ascertain the maximum reduction rate of NO that could be obtained by this new system.

Experimental Apparatus and Method

Basic Reaction Experiment

The flowsheet of the experimental system is shown in Figure 2. The flue gas, including CO, H_2, and soot, was produced from the small combustor where both methane-air premixed and diffusion flames could be formed. NO gas was introduced at point 12 on the way to the reactor. The reactor temperature could be controlled in the range of 500 to 1,200°C by the electrical furnace 3. The flue gas from the reactor passed through the filter 4, a vacuum pump, and was lead finally to the gas meter. The reduction rate of NO could be obtained from the difference of NO concentration across the reactor. A water-cooled quartz gas sampling probe with O.D. = 3.5 mm and I.D. = 2 mm was used. The chemiluminescent method of analysis was used to measure NO. Stable species such as H_2, O_2, CH_4, and CO were analyzed with a gas chromatograph. The concentration of soot was measured by a cylindrical filter method. The axial temperature profile in the reactor was measured with a 3 mm CA thermocouple. For the measurement of HCN and NH_3, an ion-electrode method was used. Since NH_3 and HCN are easily absorbed in water, the sampling line was kept warm in the temperature range of 100 to 150°C by a ribbon heater.

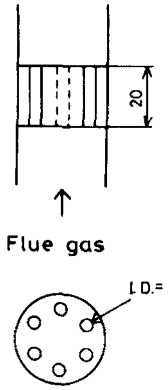

Figure 3. Arrangement of catalyst.

TABLE 1. COMPOSITION OF STAINLESS STEEL (wt.%)

C	Si	Mn	Ni	Cr	Mo
0.08	0.40	1.8	9.3	18.3	0.21

Six stainless steel catalyst pipes with I.D. = 4 mm and the length = 20 mm were set up radially in the refractory brick, as is Figure 3. This refractory brick was set in the zone of the reactor tube where the temperature profile was nearly flat.

The transformation of the stainless steel pipe to the catalyst was carried out by the following two methods. The first one is a carbon-reducing method. A stainless steel pipe whose composition is shown in Table 1 is embedded in the fluidized bed where active carbon particles with dia. = 100 μm are fluidized with the bed height = 20 cm. The bed temperature is kept at 900°C. After the stainless steel pipe is kept in the bed for 6 h, it is taken out and quenched by water. The second one is a gas-reducing method. A stainless steel pipe is kept in contact with the high temperature reducing gas where the concentration of H_2 is more than 2% and the gas temperature is about 900°C. In this case the stainless steel pipe is gradually changed to the catalyst within 10 h.

Experiment for Practical Application

The flowsheet of the experimental system is shown in Figure 4. The flue

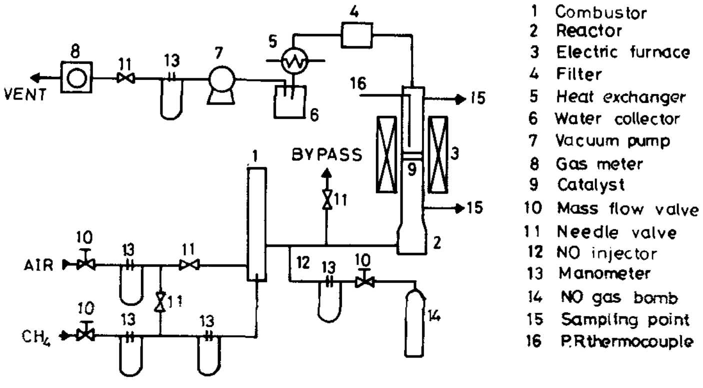

Figure 2. Flowsheet of the basic experimental system.

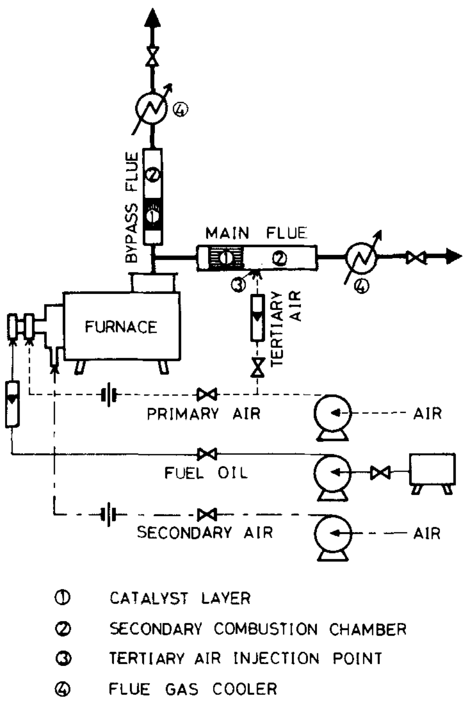

Figure 4. Flowsheet of experiment for practical application.

gas from the furnace flew mainly into the secondary combustion chamber and partly branches to the bypass flue. The residence time of the flue gas in the test section of the secondary combustion chamber could be varied from 2 to 3 s by controlling the flow rate to the bypass flue. The refractory-lined horizontal furnace employed had an I.D. of 460 mm and a length of 1,500 mm. The burner employed was a normal external air-mixing type burner in which high velocity primary air was used for atomization of the fuel. The burner thus was not a low-NOx type. The secondary combustion chamber was made of stainless steel, I.D. = 250 mm. The inside of the tube wall was covered with a refractory fiber sheet to protect the stainless steel wall from corrosion and catalytic reaction. The heat loss from the secondary combustion chamber could be kept below 20% by this fiber sheet. The tertiary air injection port was radially set at point 3 in Figure 4. The I.D. of the nozzle could be changed from 3 to 15 mm. The conditions of fluid mechanics could be changed by changing the number of nozzles and their inner diameters. The points for gas sampling and temperature measurements were positioned at 10 cm intervals. The stainless steel honeycomb was put at both the bypass side 1 and the main stream side 2; the reduction rate of NO was monitored by changing the residence time and gas composition. The catalysts, made of 4 cm long stainless steel tubes with I.D. of 8 mm in one case and 6 mm in another, were bundled as in Figure 5. The space velocity at this catalyst layer was $1.8 \times 10^5\ h^{-1}$ to $3.6 \times 10^5\ h^{-1}$. The measurement of temperature was carried out by a 0.3 mm Pt-13% Rh/Pt thermocouple covered with an insulating ceramic tube.

The fuel employed for our experiment was a heavy oil whose properties are given in Table 2. In order to simulate the emission of fuel NO, pyridine of 2.5 wt. % corresponding to 0.5 wt. % N was premixed with the heavy oil. Supposing that pyridine of 2.5 wt. % was completely converted to NO at the stoichiometric combustion condition, the calculated concentration of NO in the flue was approximately 700 ppm.

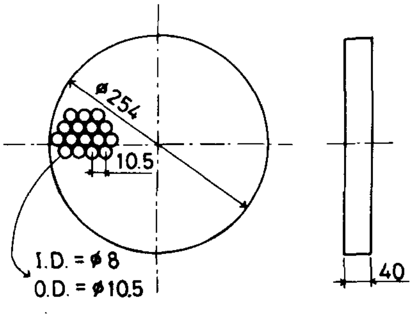

Figure 5. Details of the stainless steel honeycomb catalyst layer.

TABLE 2. PROPERTIES OF FUEL

Specific gravity (15/4°C) (kg/l)	0.847
Calorific value (kcal/kg)	10860
Flash point (°C)	78
95% Distillation point (°C)	333
C (wt.%)	85.7
H (wt.%)	13.9
S (wt.%)	0.76
N (wt.%)	0.0135

RESULTS OF THE BASIC REACTION EXPERIMENT

Reduction of NO by the Pretreated Stainless Steel Catalyst

Reduction of NO by the pretreated stainless steel is compared with the nontreated stainless steel in Figure 6. A reduction rate of 90% was obtained in the case of the treated catalyst when the catalyst temperature was 800°C and the contact time was 8 ms, while the nontreated catalyst had no significant effect on the level of NO. This result shows that pretreatment under reducing conditions is required for the stainless steel to have any catalytic effect on the reduction of NO.

Effect of Temperature at the Catalyst Layer

In order to know the effect of temperature on the reduction of NO by the stainless steel catalyst, the temperature of the catalyst layer was varied from 500 to 900°C, keeping the gas catalyst contact time constant (=10 msec). The result is shown in Figure 7. Although the reduction rate was decreased as the temperature was decreased, a reduction rate of 50% could still be maintained at 625°C.

Effect of H_2 on the Reduction of NO

The reduction effect of H_2 alone was examined by using a simulated flue gas (H_2: 2.7%, N_2: 97.3%, NO: 900 ppm) instead of a combustion flue gas. The result is shown in Figure 8. It should be noticed that the correlation between the NO residual rate (1 − the NO reduction rate) and the contact time is similar to that of combustion flue gas (Figure 6). This result suggests that the contribution of H_2 in the flue gas is significant for the reduction of NO.

Conversion of NO into HCN and NH_3

If NO is mostly converted to NH_3 or HCN by the stainless catalyst at the primary stage, these species are partly converted to NO again by the introduction of the tertiary air in the secondary stage of combustion. So it was required to analyze NH_3 and HCN in the

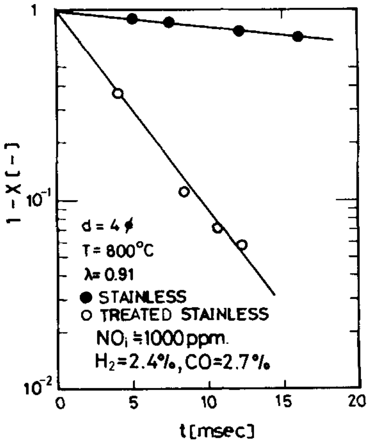

Figure 6. Comparison between treated and nontreated stainless steels.

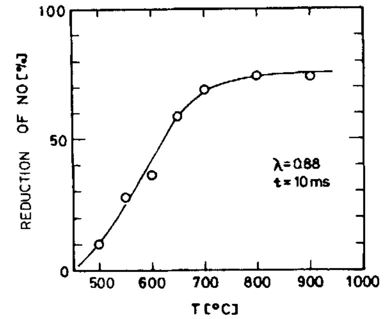

Figure 7. Effect of catalyst temperature on the reduction of NO.

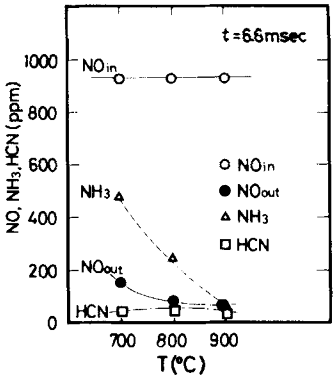

Figure 9. NO, HCN, and NH_3 at outlet of the catalyst layer.

flue gas at the outlet of the catalyst layer in order to make clear whether this stainless steel catalyst was useful in the two-stage combustion.

The level of NO, HCN, and NH_3 at the outlet of the catalyst layer is plotted against the catalyst temperature in Figure 9 when the contact time was 6.6 msec and actual flue gas was used as the reducing gas. The conversion rate of NO into NH_3 decreases from 50 to 5%, corresponding to the temperature increase from 700 to 900°C. On the other hand, the conversion rate of NO into HCN was approximately 5% and independent of temperature. These results indicate that when the catalytic temperature is 700°C, a quarter of the initial NO must be recovered at the secondary combustion if the conversion rate of NH_3 into NO is assumed to be 50%. It means that the final reduction rate would become 75% even if the reduction rate of NO at the exit of catalyst layer is 100%. On the other hand, nearly complete reduction of NO can be expected when the catalytic temperature is 900°C, as the conversion rate of NO into NH_3 is only 5% at this temperature.

Reduction Mechanism of NOx

From the result that the contribution of H_2 in the flue gas is significant for the reduction of NO, an overall reaction scheme for reduction of NO on the stainless steel catalyst might be

$$NO + H_2 \rightarrow \frac{1}{2} N_2 + H_2O \qquad (1)$$

However, from the result that nearly half of NO is converted to NH_3 at 600°C, the following reaction scheme has to be taken into account as well:

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \qquad (2)$$

In order to examine the reduction mechanism of NO more exactly, the following experiments were carried out.

1) Initially, a $H_2/NO/N_2$ gas mixture was passed through the catalyst layer until sufficient reduction of NO was confirmed. Then H_2 was excluded from the gas mixture and the behavior of NO at the outlet of catalyst layer was observed.

2) In the above experiment, O_2/N_2 mixture gas was passed through the catalyst layer for a short period before $H_2/NO/N_2$ gas was changed to NO/N_2 gas.

In the first experiment it was noticed that the reduction rate of 50% was still effective 20 min after H_2 had been removed; this is shown by the recovery curve of NO at the outlet of catalyst layer in Figure 10. This result suggests that oxygen from NO was being trapped by the oxygen defect on the stainless steel surface, which might have been produced by the action of H_2. In the second experiment NO was not reduced at all once the stainless steel catalyst was contacted with O_2 after the removal of H_2. This implies that oxygen defects made by H_2 were filled again by oxygen and consequently no reduction of NO took place afterward.

From these results, the so-called "Redox" mechanism is likely to happen as the reduction mechanism. That is,

$$\text{Me-O-Me} + H_2 \rightarrow \text{Me-}\square\text{-Me} + H_2O$$

$$\text{Me-}\square\text{-Me} + NO \rightarrow \text{Me-O-Me} + \frac{1}{2} N_2$$

where

Me : Metal

□ : Oxygen defect

In the practical system, NO and H_2 would not behave separately as is suggested by the redox mechanism. Sometimes active N, which may be formed from the reduction of NO, reacts with coexistent H_2 to form NH_3, NH_2, or NH. The ammonia radicals are likely to cause homogeneous reduction of NO in the gas phase under the high temperature condition. The details of this homogeneous reaction mechanism will be reported elsewhere.

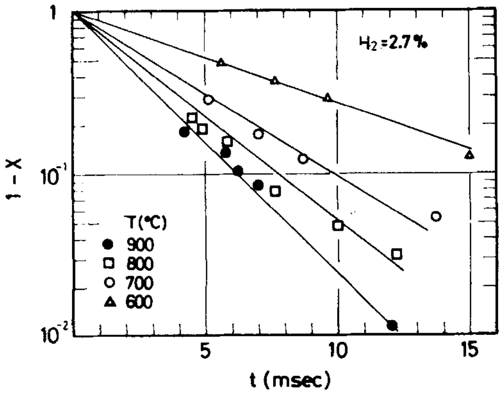

Figure 8. Reduction of NO in a simulated flue gas.

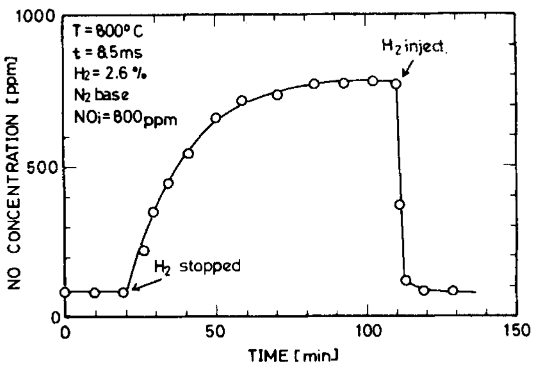

Figure 10. Recovery curve of NO at the outlet of the catalyst layer.

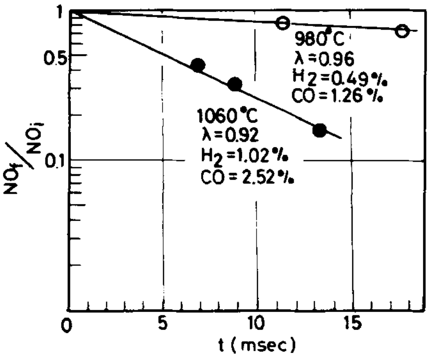

Figure 11. Effect of pretreatment time on catalytic reduction of NO.

Corrosion Resistance of the Stainless Steel Catalyst in the Reducing Atmosphere

The corrosion resistance of the stainless steel catalyst was investigated as follows. First, the catalyst was repeatedly used under the reducing gas condition (2.3% H_2/3.5% CO/N_2) for 250 h. There were no signs of deterioration throughout the test. Next, the corrosion resistance of this catalyst was tested by using the reducing gas including high concentration SO_2 (1000 ppm SO_2/2.3% H_2/3.5% CO). Although the reduction rate of NO was decreased from 90 to 80% initially, there was no change of activity for more than 100 h afterwards. The same test was carried out for the carbon-steel and pure iron. It was shown that both the carbon-steel and pure iron became brittle within several hours in the reducing atmosphere as compared with the stainless steel catalyst.

In order to investigate the mechanism of the corrosion resistance and mechanical strength of the stainless steel catalyst, the concentration distribution of the metal compound in the stainless steel, such as Fe, Ni, and Cr, on the cross section of the catalyst was examined using an XMA (X-ray microanalyzer). The result was that a thin layer of high concentration nickel could be observed at approximately 20 μ from the surface of the treated stainless steel catalyst while nickel was homogeneously distributed in the nontreated catalyst. Therefore, this high concentration nickel layer is likely to protect the catalyst from the corrosion and physical destruction. However, the iron layer surrounding the nickel-rich layer seemed to become more porous with repeated reduction-oxidation operations. Thus this stainless steel catalyst should be used continuously in a reducing atmosphere once a sufficient activity has been obtained by several reduction-oxidation operations.

From the above observations, it may be conjectured that an initial reduction-oxidation operation contributes to the activation of the stainless steel through an increase of the specific surface area and the formation of a nickel-rich layer.

RESULTS OF THE EXPERIMENT FOR PRACTICAL APPLICATION

Pretreatment by Reducing Flue Gas

On the basis of the previous results, experiments using the medium size two-stage combustion furnace equipped with the stainless steel honeycomb catalyst were planned and carried out. In these experiments pretreatment of the catalyst by high temperature reducing flue gas was adopted instead of carbon since the pretreatment by reducing gas was easier than that by carbon.

The results are shown in Figure 11, where the key (○) indicates NO reduction rate by the stainless steel honeycomb when the pretreatment time was only few minutes in the flue, while the key (●) indicates the result when the pretreatment time of the stainless steel was 24 h. The catalyst temperature in the latter case was a little higher than that of the former. It is shown that the stainless steel honeycomb, which did not show the catalytic effect initially, was converted to the catalyst after it had been kept in the reducing flue gas for 24 h.

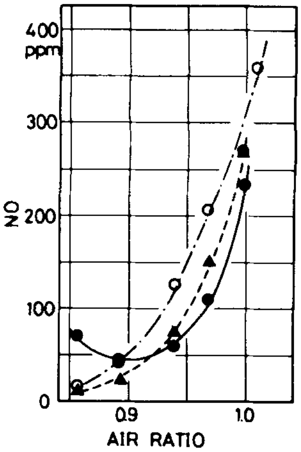

Figure 12. Demonstration experiment of catalytic two-stage combustion.

○ = NO at primary stage

▲ = NO at outlet of catalyst layer

● = NO after secondary combustion

Demonstration Experiment of NOx-Free Combustion System

As the optimum condition for the reduction of NO had been found by the basic experiment, the demonstration experiment was carried out to check whether the final NO level could be controlled under 50 ppm and whether the complete combustion of unburnt species was possible. The measurements of NO, CO, H_2, and soot concentrations were made at the furnace outlet, the outlet of the catalyst layer, and the outlet of the secondary combustion zone. In this experiment the gas-catalyst contact time was 10 msec, which corresponds to SV = 3.6×10^5 h^{-1} and the catalyst temperature was 1000°C. The flow rate of the secondary combustion air injection from the single nozzle with I.D. of 9 mm was adjusted so that the final air ratio became 1.05.

The result is shown in Figure 12, where the key (○) indicates NO at the primary stage, the key (▲) indicates NO at the outlet of the catalyst layer, and the key (●) indicates NO after the secondary stage of combustion. These results show that NO is reduced more than half across the catalyst layer and its further reduction is achieved by the injection of the secondary combustion air when air ratio is more than 0.93. On the other hand, NO was slightly increased by the injection of the secondary combustion air when the primary air ratio was less than 0.93. As a result, the minimum level of NO was 48 ppm at an air ratio of 0.90. This level corresponds to a reduction rate of 93%, as the ordinary NOx level of this system is about 600 ppm, which is the sum of 150 ppm fuel NO and 450 ppm thermal NO at air ratio = 1.05. The decrease of NO in the primary air ratio range over 0.93 cannot be explained only by the dilution effect due to the secondary combustion air injection. As NH_3 is easily converted to NHi (ammonia radicals) in the presence of O_2, the reduction of NO by ammonia radicals may take place in this range. Lyon (1976) showed that ammonia radicals easily attack NO and convert it to N_2. On the other hand, the increase of NO converted from NH_3 would exceed its reduction by NH_3, where the NH_3 level is higher than the NO level. This might be the main cause for the increase of NO in the primary air ratio range under 0.93.

Measurements of CO, H_2, and soot after the secondary combustion showed that these unburnt products were completely burnt in the secondary combustion. Thus it was demonstrated that NO

= 50 ppm, which was the final target of our study, was mostly attained, and the complete combustion of unburnt species was possible. The space velocity of this catalytic system, SV = 3.6×10^5 h^{-1}, is at least 10 times as high as that of the conventional selective catalytic reduction process in which NH_3 is used as reducing agent and the space velocity is 10^4 h^{-1} at most (Atsukawa et al., 1977).

ACKNOWLEDGMENT

The work presented in this paper was supported by the Fund Inc. for Technological Development for Abatement and Removal of NOx from Steel Plants.

NOTATION

d = inner diameter of catalyst
t = contact time
T = temperature
X = reduction rate of NO
λ = air ratio

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Manuscript received Oct. 5, 1982; revision received June 5, 1984, and accepted June 8.