Study of Catalytic Reduction of NO_x in Flue Gas from a Municipal Refuse Incinerator* (Experimental Results of NO_x Removal Test Plant)

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The catalytic reduction process of NO_x by NH₃ has been applied mainly to the clean combustion flue gases of LPG or LNG, which do not contain the harmful component which reduces the catalyst activity. This paper describes the experimental results of a survey for the catalytic reduction removal of NO_x from dirty gas containing higher concentrations of HCl, SO_x and dust emitted from a municipal refuse incinerator. The effects of reaction temperature, space velocity and the amount of NH₃ injection on the NO_x removal efficiency are studied experimentally, and the change of V₂O₅-TiO₂ catalyst performance with time is examined; and the regeneration techniques for catalysts are also discussed on the basis of the results of the heat treatment.

Key Words: Combustion, NO_x Removal Test Plant, Pellet Catalyst Reactor, Removal Efficiency, Flue Gas, Municipal Refuse Incinerator

1. Introduction

Recently the removal technique of NO_x in flue gas from a municipal refuse incinerator has become a great concern in relation to the regulation of total nitrogen oxide (NO_x) emission in urban areas. Between 80 and 100 ppm (converted at 12% O₂) will be considered as a target emission standard. To attain this standard, the selective non-catalytic reduction of NO_x⁽¹⁾ and flue gas recirculation^{(2),(3)} are successfully applied; but in preparation for the possible requirement of regulation to less than 50 ppm in the future, research into the catalytic reduction of NO_x is required. This technique has been used mainly for the reduction of the NO_x of clean flue gas from an LPG fired boiler in the past, but recently this technique has been experimentally used to clean dirty gas containing catalytic poisons and dust such as flue gas emitted from a municipal refuse incinerator⁽⁴⁾⁻⁽⁷⁾. However many problems such as the deterioration of catalytic performance and regeneration technique for the cata-

lyst remain unsolved for practical application; that is, the effect on the catalytic reduction performance of reaction products of sulfur oxides and hydrogen chloride in a flue gas with ammonia used as a reducing agent, and the effects of metal sulfates, and metal chlorides.

In this paper, to obtain the optimal condition in the application of the catalytic reduction of NO_x to flue gas from a municipal refuse incinerator, the effect of temperature, amount of reducing agent, flow rate of flue gas, and amount of catalyst on the reduction of NO_x was investigated using a flue gas dry NO_x reduction test plant which was developed by the authors, to which practical flue gas was introduced. The poisoning of catalyst, regeneration, life, and dust clogging were also considered.

2. Experimental Apparatus and Procedure

This experiment was conducted in a refuse incinerator plant. The flow of the experimental apparatus is shown in Fig 1. From 80 to 150m³/h at STP (standard temperature and pressure, 0°C, atmospheric pressure) of flue gas was drawn out at a position beyond an electrostatic precipitator (EP) of the municipal refuse incinerator, introduced into the NO_x reduction equipment by a forced draft fan (FDF), and

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forced to pass through an electric heater (30 kW), ammonia mixer (with spray nozzles), and a pellet catalyst reactor; then the flue gas was returned to a duct of the incinerator at a position beyond an induced draft fan (IDF) through an orifice to measure the flow rate.

The catalyst reactor and pipes to and from it were covered with thermal insulator to reduce heat loss. The pellet catalyst reactor had a two-step layer structure, and a by-pass air pipe was provided on the inlet side of the FDF to perform a regeneration experiment with the catalyst (flow of hot air at 350 to 400°C for several hours). EP outlet flue gas contained on average 70 to 110 ppm of NOx, 7 to 11% of O₂, 20 to 40 ppm of SOx, 200 to 400 ppm of HCl, 20 to 30 mg/m³ at STP of dust, and 30 to 35% of H₂O, and the temperature ranged from 350 to 280°C. The NOx reduction catalyst used in this experiment comprised TiO₂ carrier, which displays high performance and durability regardless of the presence or absence of SOx, and V₂O₅ active material; the diameter of the catalyst pellets was 5 mm.

The experiment was carried out at reaction temperatures in the range of 240 to 350°C, 4 400 to 12 500 h⁻¹ in space velocity (flue gas flow rate m³/h at STP / volume of catalyst bed m³, SV-value), and 0.3 to 0.43 m/s at STP in the linear velocity of the reactor; and the amount of ammonia injection was varied. In the case of the life test, one catalyst layer was used, and a reaction temperature of 240°C was utilized in consideration of practical operation; and experimental conditions of SV=8 800 h⁻¹ and NH₃/NOx=0.5 to 2.5 (in molar ratio) were used. In Fig. 1, positions for temperature measurement and sampling of flue gas are shown. Samples of flue gas were analyzed continuously for O₂ by the magnetic induction method, for CO and CO₂ by infrared gas analysis, and for NOx by chemiluminescent reaction analysis. NH₃ was sampled for 30 min. from flue gas in one experiment, and the concentration was determined manually by quantitative analysis using the indophenol method (JIS K 0099). The temperature of the flue gas was measured with a K-thermocouple. To determine the de-

Fig. 1 Experimental apparatus

rioration of the catalyst, the catalyst was sampled at regular intervals and after-and-before catalyst regeneration; then, values which relate to the deterioration of catalyst activity, such as specific surface area of the catalyst (m²/g, BET method), micro pore volume (ml/g, mercury porosimetry method), SO₄²⁻ (in weight %, ion chromatography), and Na⁺ and K⁺ (in weight %, atomic absorption spectrochemical analysis) were measured and analysed.

3. Experimental Results and Considerations

In Fig. 2, an example of O₂ and NOx measurement results before and after treatment with the catalyst reactor is shown. The molar ratio NH₃/NOx changes from 0.79 to 1.07 as the NOx concentration ① at the inlet varies depending on the change in characteristics of refuse with the same ammonia injection amount during the AB period on the axis of the abscissa. The inlet NOx concentration ① of the catalyst reactor varies violently, but the outlet NOx concentration ② varies over a considerably small range for the constant feeding of NH₃. The reason for the fact is thought to be that excessive NH₃ is absorbed on the catalyst when NOx concentration is small; and on the contrary, NH₃ is released from the catalyst to contribute to the NOx reduction. The catalyst has the preferable performance described above to compensate for the load variation; thus when this NOx reduction system is utilized by commercial plants, only a constant NH₃ feeding system may be used. This performance is very favorable for this kind of catalytic reduction process. The ammonia injection amount was reduced at the point of B in Fig. 2. After the point B it requires a considerable period of time to observe the reduction in removal efficiency ((inlet NOx concentration-outlet NOx concentration)/inlet NOx concentration in %), this result also possibly corresponds to the absorption and disconnection of

Fig. 2 Example of O₂ and NOx measurement results

Fig. 3 Pressure loss change with time in the catalyst reactor

Fig. 4 Relation between NOx removal efficiency and NH_3/NO_x

excessive NH_3 .

In Fig. 3 the pressure loss change with time in the catalyst reactor is shown. The time when the initial pressure loss increases to five times ranges from 200 to 690 hr. However the time is possibly different depending on the characteristics of dust.

In Figs. 4 and 5, experimental results which show the relation between NOx removal efficiency, NH_3/NO_x (molar ratio), SV-value, and reaction temperature are presented. From the figures it is obvious

Fig. 5 Relation between NOx removal efficiency and NH_3/NO_x

that the NOx removal efficiency decreases with increased SV-values under the condition of $\text{NH}_3/\text{NO}_x > 1$, the NOx removal efficiency increases with increasing of reaction temperature, and the reaction between NH_3 and NO proceeds approximately according to an equimolar reaction (broken lines in Figs. 4 and 5) as shown in the following equation.

On the other hand, the measurement was carried out while the NO_2 -NO converter of the NOx concentration meter was bypassed, and from the result it is confirmed that NOx in the flue gas contains 90% or more of NO, this fact also corresponds to the formulation of the principal reaction between NH_3 and NOx by equation (1).

In Fig. 6, the value of leaked ammonia is plotted against NOx removal efficiency for the case of NH_3/NO_x in a range from 0.05 to 1.25, shown in Figs. 4 and 5. From this figure it is derived that approximately 15

ppm of leaked ammonia is contained in flue gas after passing through the catalyst reactor at an NO_x removal efficiency of 80%. Figure 7 shows the typical NO_x removal efficiency value against reaction temperature at the NH₃/NO_x injection molar ratio of 0.9 to 1.3. From this figure it is obvious that the NO_x removal efficiency retains its level as high as more than 90%, even at an SV-value of 5 800 h⁻¹, as long as the reaction temperature is high.

Figure 8 shows the NO_x removal efficiency at ammonia injection molar ratios of 1 and 0.5 for a reaction temperature of 240°C to make the effect of the SV-value more obvious, which is obtained from Figs. 4 and 5. The NO_x removal efficiency decreases approximately exponentially with increasing SV-values (in this experiment corresponding to the

Fig. 6 The value of leaked ammonia against NO_x removal efficiency

Fig. 7 Relation between NO_x removal efficiency and reaction temperature

Fig. 8 Relation between NO_x removal efficiency and space velocity

increasing flow rate of flue gas). Figure 9 shows the catalyst performance with time. From this figure it is observed that the NO_x removal efficiency decreases gradually with operational time from the initial value "1" of 78% to a value "2" of 73% after 670 hr operation. "3" in Fig. 9 represents the experimental result after 1 280 hr operation when the ammonia injection molar ratio happened to temporarily change to about 6 due to a failure of the control system. The NO_x removal efficiency decreased rapidly but recovered slightly by decreasing of the molar ratio. Therefore it is estimated from the regeneration experiment, which will be described below, that the intermediate state between "2" and "3" returns to state "4". Analytical results of catalyst and catalyst dust are shown in Fig. 10. Numbers 1 to 5 in Fig. 10 corresponds with the numbers in Fig. 9.

In one instance⁽⁸⁾, heat treatment and washing with hot water were cooperatively applied to regenerate the NO_x reduction catalyst, considering that the recovery of activity by heat treatment only is insufficient. However in this study, in order to perform regeneration most energy conservatively, the regeneration of the catalyst was carried out in such a way that when the NO_x removal efficiency decreased to 57% after 1 300 hr operation, hot air (350 to 380°C) was introduced for 150 min. This regeneration opera-

Fig. 9 Catalyst performance with time

Fig. 10 Analytical results of catalyst and dust

tion corresponds to "3" and "4" (before and after recovery) in Figs. 9 and 10, and the NO_x removal efficiency is recovered to 76% by this heat treatment.

Formerly it has been considered⁽⁵⁾ that acid ammonium sulfate (NH₄HSO₄) which results from a reaction between leaked ammonia and SO_x and covers the catalyst as dust, is vaporized by heating at 400°C to recover the specific surface area and micro-pore volume of the catalyst to fresh conditions; however in the experimental result shown in Fig. 10, catalyst deteriorating components of Na⁺, K⁺, and SO₄²⁻ decrease only slightly with heat treatment at such a temperature and contrary to the regeneration effect, the specific surface area and micro-pore volume rather decreases. The NO_x removal efficiency is recovered by several percent by heat treatment; but Fig. 10 shows that the specific area and micro-pore volume of the catalyst decreases with time: additionally, Na⁺, K⁺, and SO₄²⁻ tend to be accumulated in the catalyst. The NO_x removal efficiency after 2 350 hr of operation "5" is approximately 74%.

The effect of HCl in flue gas on the catalyst performance can not be discussed in detail because practical flue gas is used and the HCl concentration can not be changed; but when the reactor was operated with an ammonia injection molar ratio NH₃/NO_x of more than 1 for a long time, the deposit of ammonium chloride NH₄Cl was observed in the sampling pipe of the inlet side of the reactor. From this fact it is derived that when NH₃ is fed excessively, the reaction

proceeds before the reactor; and on the contrary, when NH₃/NO_x < 1, NO_x reduction reaction proceeds prior to the reaction of equation (2) because the equimolar reaction of equation (1) almost holds. When flue gas contains HCl, chlorides of heavy metals are formed. The effect of these salts on the catalyst performance will be discussed in future.

4. Conclusions

Important results obtained in this study are summarized as follows:

(1) When the ammonia injection at a molar ratio NH₃/NO_x greater than 1 the NO_x removal efficiency decreases with increasing SV-value (increasing in flow rate of flue gas), and when NH₃/NO_x less than 1 the reaction proceeds according to the equimolar reaction equation (1).

(2) The NO_x removal efficiency increases with increasing catalytic reaction temperature, and even under the practical reaction temperature of 240°C the NO_x removal efficiency of 80% or more can be obtained (NH₃/NO_x ≥ 1) with SV-value of 8 000 h⁻¹ or

less, when leak ammonia is 15 ppm or less.

(3) At a reaction temperature of 240°C and an SV-value of 8 800 h⁻¹ the NO_x removal efficiency tends to decrease gradually during 2 500 hr operation. This result is confirmed by analyzing the properties and catalyst dust of the catalyst. To consider the possibility of catalyst regeneration, a regeneration experiment in which hot air of 350 to 380°C was introduced for 2 to 3 hr to the reactor was tried and the recovery of several percent of NO_x removal efficiency was obtained; but on the other hand, depending on the results of measurement and chemical analysis on the catalyst before and after regeneration and catalyst dust, a result suggesting that the regeneration effect can not be expected with heat treatment at such temperature for such a treatment period is obtained. From this experimental result it must be asked what is the catalyst poisoning substance?. Remarkable corrosion was not observed on the piping system during this experiment.

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