

## Catalytic process for decolorizing yellow plume

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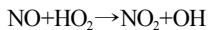
**Abstract**—Yellow-colored exhaust gas streams from internal engines or gas turbines, frequently referred to as “yellow plume,” contain nitrogen dioxide ( $\text{NO}_2$ ) at concentrations as low as 15 ppm. The process developed in this work for decolorizing the yellow plume is based on reduction of  $\text{NO}_2$  to  $\text{NO}$  utilizing a combination of a Pt catalyst and a reducing agent. A stoichiometric excess of carbon monoxide, diesel oil, methanol or ethanol were used as reducing agents. Depending on the type of the reductant, the active temperature window of  $\text{NO}_2$  reduction was varied with methanol and CO being active at lower temperatures and ethanol and diesel oil at higher temperatures. By changing the Pt loading of the catalysts the active temperature window of  $\text{NO}_2$  reduction was also changed, higher loading Pt catalysts being active at lower temperatures. This scheme of  $\text{NO}_2$  reduction process was verified in a pilot-scale test with the real exhaust gas from the gas turbine power plant, showing 96% of  $\text{NO}_2$  reduction at the stack temperatures of 102–123 °C and at space velocities of 28,000–95,000  $\text{h}^{-1}$  with inherent CO in the exhaust gas as the reducing agent.

Key words: Yellow Plume, Decolorizing,  $\text{NO}_2$  Reduction, Pt Catalyst, Pilot Scale

### INTRODUCTION

Most stationary sources such as boilers, gas turbines and internal engines emit nitrogen oxides. Nitrogen oxides, generally defined as the formula  $\text{NO}_x$ , include  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_5$  and  $\text{N}_2\text{O}$ . Of all the  $\text{NO}_x$ , only  $\text{NO}_2$  has a brown color. The exhaust stream containing even 15 ppm of  $\text{NO}_2$  may show a yellow color from large diameter stacks [1]. The yellow-colored exhaust stream is frequently referred to as “yellow plume.” The  $\text{NO}_2$ -induced yellow plume causes not only smog, ozone generation ( $\text{NO}_2 + \text{O}_2 + \text{ultraviolet rays} \rightarrow \text{NO} + \text{O}_3$ ) and harmful health effects but also the visible fear of nearby residents. Thus, the sources of the yellow plume are in need of an efficient process which can decolorize the yellow plume to avoid the possible law suits by the residents.

$\text{NO}_2$  formation has been reported to take place through “ $\text{HO}_2$  mechanism” as shown below [2]:



An unusually high concentration of  $\text{NO}_2$  is formed in the areas of large temperature gradients in the flame, the periphery of the flame where the hot combustion gases mix with cool surrounding air. There is a temperature window between 530 °C to 730 °C in which  $\text{NO}$  to  $\text{NO}_2$  conversion occurs readily [3]. The presence of unburned fuel or other oxidizable species such as CO is also known to promote the formation of  $\text{NO}_2$  [3].

Three major approaches have been used to reduce  $\text{NO}_x$  emissions: (1) precombustion modifications such as switching fuels and denitrifying the fuel; (2) combustion modification such as changing oxygen concentration and lowering the combustion temperatures; and (3) postcombustion treatment. Considering the cause of formation and the low level of the  $\text{NO}_2$  concentration to bring out a yellow

color, precombustion and combustion modifications may not be effective in achieving the decolorization of the yellow plume exhaust. The decolorization can be easily achieved by postcombustion treatments since reduction of  $\text{NO}_x$  to the ppm level is frequently practiced by postcombustion treatments.

Since 1960s the method of nonselective catalytic reduction (NSCR) of  $\text{NO}_x$  including  $\text{NO}_2$  in the exhaust from nitric acid plants has been applied [4]. Oxygen contained in the exhaust stream is first removed by combusting natural gas or LPG.  $\text{NO}$  and  $\text{NO}_2$  in the resultant oxygen deprived stream is reduced to nitrogen with the remaining fuel or with the byproduct from the combustion ( $\text{CH}_4$ ,  $\text{H}_2$  and CO, etc) over the catalyst bed. The catalyst is made of 0.3–0.5% Pt and a small amount of Rh on alumina in a honeycomb shape. Depending on the type of the reductant, the operating temperatures are varied: 300–350 °C for  $\text{H}_2$  and CO and 500–550 °C for natural gas. A similar process to NSCR is revealed in the U.S. patent [5] with the following procedure. The mixture of  $\text{NO}_x$  containing exhaust stream and fuel passes through an afterburner to remove all the oxygen. After the temperature of the stream is lowered in a heat exchanger, a small amount of air is injected to the oxygen-deprived stream.  $\text{NO}$  in the resultant stream is oxidized to  $\text{NO}_2$  in the first section of the catalyst bed and all  $\text{NO}_2$  is reduced to nitrogen with a small amount of excess fuel in the second section of the catalyst bed. The remaining unreacted fuel is oxidized over the final oxidation catalysts. Both NSCR processes and the process are revealed in the U.S. patent [5] are costly processes since they need significant amounts of fuel to consume all the oxygen present in the exhaust stream.

Selective catalytic reduction (SCR) of  $\text{NO}_x$  using ammonia as a reducing agent is considered one of the most effective processes for removing  $\text{NO}_x$  from flue gases [6,7]. The ammonia SCR processes utilizing titania supported vanadia catalysts achieves up to 90% of  $\text{NO}_x$  conversions at temperatures ranging from 200 °C to 400 °C. However, the process suffers from problems of forming

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$\text{NH}_4\text{HSO}_4$  causing corrosion and plugging of the reactor and large equipment and operating costs associated with storage, delivery and use of ammonia in the process.

Numerous efforts have been made to replace ammonia with hydrocarbons in SCR processes, especially in an oxygen-rich environment [8-10]. Many types of hydrocarbons have been tested including methane, ethane, ethylene, propane, propylene, octane, benzene, acetone, cyclohexane, diesel oil, methanol, and ethanol. A wide variety of materials show catalytic activity including zeolites [11], ion exchanged zeolites [12] and supported metal catalysts [13]. Most of the efforts have been concentrated on reducing  $\text{NO}_x$  to  $\text{N}_2$  at temperatures higher than 200 °C but with limited success. However, the catalytic reduction of  $\text{NO}_2$  for the specific purpose of decolorization of the exhaust stream has not been reported.

In addition, a large portion of exhaust stream with a yellow color is vented at temperatures of about 100 °C. For example, the stack gas temperature of a natural gas and/or oil fired combined cycle power plants after the combustion gas passing through a heat recovery steam generator (HRSG) ranges between 100 °C to 150 °C. The exhaust gas temperature from particulate control devices such as electrostatic precipitators or bag filters of coal fired facilities is around 100 °C. No successful result of catalytic reduction of  $\text{NO}_x$  including  $\text{NO}_2$  at temperatures of about 100 °C has been reported. If the ammonia SCR process were to be employed in the existing plant for the purpose of removing yellow plume, the gas stream with the right temperature range (200-400 °C) in the process flow has to be pinpointed and to be diverted to go through an SCR reactor. It will require both significant amounts of ductwork and the space for the SCR reactor. An alternative way is to burn additional fuel to raise the stack gas temperature to 200-400 °C, and then to pass the heated gas through the SCR reactor. Heat exchangers can be employed to recover heat from the SCR reactor effluent before venting it to the air. Both options require large capital and operating costs.

The most cost efficient way of decolorizing yellow plume is to utilize a process which operates at exhaust gas temperatures obviating additional heating/cooling devices and the corresponding fuel costs. Additional advantage can be obtained if the process can be operated in oxygen-rich environments with cheaper hydrocarbon type or carbon monoxide reducing agents.

In this work we report a process that can selectively reduce yellow-color-inducing  $\text{NO}_2$  in the exhaust gas stream with oxygen present at temperatures close to 100 °C and higher with the combination of Pt catalysts and non-ammonia reducing agents, ensuring an economic way of having colorless exhaust stream vented to the atmosphere.

## EXPERIMENTAL

The honeycomb-type Pt impregnated on alumina catalysts was prepared by the incipient wetness method. The ceramic monolith (Corning, Inc.) was dipped into the slurry of porous alumina particles (Aldrich,  $\gamma\text{Al}_2\text{O}_3$ , surface area: 170 m<sup>2</sup>/g) and then dried several times until the desired amount of alumina was washcoated. Based on the weight of the ceramic honeycomb monolith, about 15 wt% of alumina was washcoated on the monolith. After the calcination of the dried catalyst in air at about 600 °C for 12 hours, the alumina-washcoated monolith was dipped into the aqueous solution

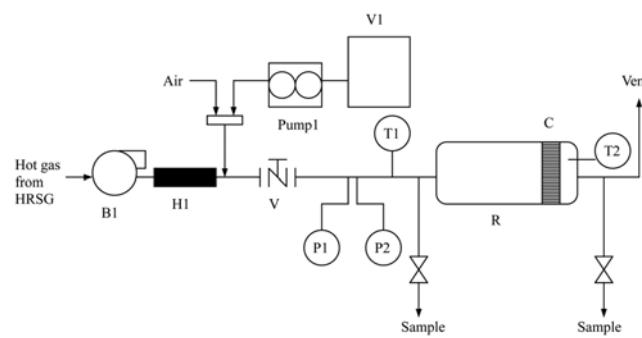
of hydrogen hexachloroplatinate ( $\text{H}_2\text{PtCl}_6$ ) at 25 °C. The concentration of  $\text{H}_2\text{PtCl}_6$  was adjusted such that the desired loading of Pt in the final catalyst was obtained. The Pt-containing monolith was dried at 110 °C for 4 hours and recalcined at 500 °C in air (6 hours). The calcined catalyst underwent the hydrogen treatment at the elevated temperature (450 °C, 4 hours) to ensure Pt particles in a reduced metallic form.

The catalysts thus obtained contained 0.001 to 0.33 wt% Pt (based on the total weight of the catalyst including the monolith). The content of Pt in the catalyst was measured by the PIXE (proton induced x-ray emission; manufactured by Korea Institute of Geology and Mineralogy with NEC 5SDH-2 accelerator).

The type of the reducing agent ranged from the inherent gas in the exhaust (CO) to liquid fuels (diesel oil, methanol and ethanol). The amount of reducing agent to be added to the  $\text{NO}_2$ -containing flue gas was varied in that molar ratio of carbon/ $\text{NO}_2$  changed from 2 to 8.

Two different sets of experiments were carried out at different scales of the catalyst volume and the gas flow rate. The first set of experiments was run to screen both the catalyst and the reducing agent in a small-scale unit. The reactor was constructed with a stainless steel tube (inside diameter of 6 cm and length of 14.5 cm). A separate heated inlet for admixing both the liquid reducing agent and water with premixed gas containing  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{O}_2$ ,  $\text{CO}_2$  and  $\text{N}_2$  was provided at the position where thorough mixing took place before the mixture contacts the catalyst. Both water and the liquid reductant were supplied by a multiple syringe pump. The catalysts used in the test were 2 cm×2 cm×3 cm size honeycomb type with the cell density of 400 cells per square inch (cpi). The composition of the simulated inlet gas was 120 ppm  $\text{NO}_2$ , 20 ppm  $\text{NO}$ , 16%  $\text{O}_2$ , 2.5%  $\text{CO}_2$ , 5%  $\text{H}_2\text{O}$  and balance  $\text{N}_2$ . The typical gas hourly space velocity was 12,500 h<sup>-1</sup>. The product analysis during the activity measurements was made using an online flue gas analyzer (Green-Line Mk 2, Eurotron).

A larger reactor constructed with a stainless steel tube (inside diameter of 89 cm and length of 123 cm) was used in the proof-of-concept runs (Fig. 1). The real gas turbine exhaust gas showing the yellow color was introduced to the reactor at varying flow rates by



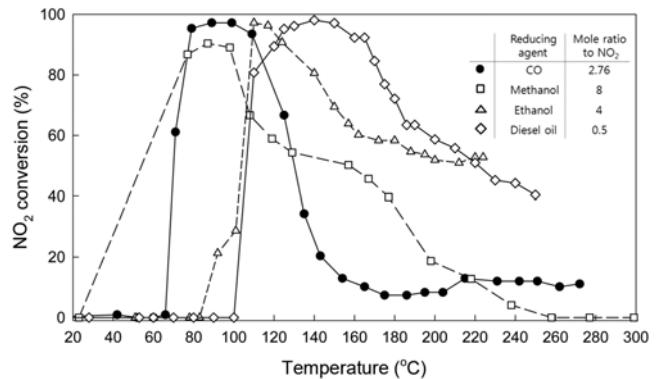
**Fig. 1.** Schematic diagram of pilot-scale yellow plume decolorization experimental unit (B1: blower, H1: electric heater, V: valve, Pump1: metering pump, V1: methanol storage vessel, T1: thermocouple for inlet temperature measurement, P1, P2: pressure transducers for pitot tube, T2: thermocouple for reactor exit temperature measurement, R: reactor, C: catalyst).

a blower equipped with a valve. Methanol was introduced to the gas stream before the reactor as the reducing agent. When inherent CO was to be used as a reducing agent, no other reducing agent was added to the gas stream. Two different loading of Pt impregnated catalysts were used: 0.22 wt% (200 cpi, 4,500 cm<sup>3</sup>) and 0.27 wt% (400 cpi, 9,000 cm<sup>3</sup>). The catalyst was placed at the rear end of the reactor. The typical composition of the inlet gas was 24 ppm NO<sub>2</sub>, 15 ppm NO, 17% O<sub>2</sub>, 2.0% CO<sub>2</sub>, 4% H<sub>2</sub>O, 360 ppm CO and balance N<sub>2</sub>. The temperature of the exhaust gas was about 120 °C, but the electrically heated pipe was used in case of raising the temperature of the gas entering the reactor. The gas hourly space velocity was varied from 28,000 h<sup>-1</sup> to 95,000 h<sup>-1</sup>. The flow rate of the exhaust gas was measured by pitot tubes with pressure transducers.

## RESULTS AND DISCUSSION

### 1. Yellow Plume Phenomenon

When the exhaust gas contains NO<sub>2</sub>, it may show yellow color depending upon both the concentration of NO<sub>2</sub> and the diameter of the stack. Fig. 2 shows pictures of the color of the exhaust gas vented from the stack of a gas turbine-fired power plant in the Republic of Korea during the start-up period. As the power output of the gas turbine was increased from 0 to the steady state output of 80 MW, the yellow color was observed at the output from 10 MW to 50 MW, but the color disappeared at output higher than 60 MW. The gas composition was measured with GreenLine MK2 gas analyzer (Eurotron) during the start-up period and the results are also shown in Fig. 2. As can be seen, the concentration of NO<sub>2</sub> was higher than 30 ppm during the power output between 10 MW and 50 MW, when the yellow color was clearly visible. However, the NO<sub>2</sub> concentration decreased to about 10 ppm at the output higher than 60 MW when the yellow color disappeared. The result in Fig. 2 clearly shows that



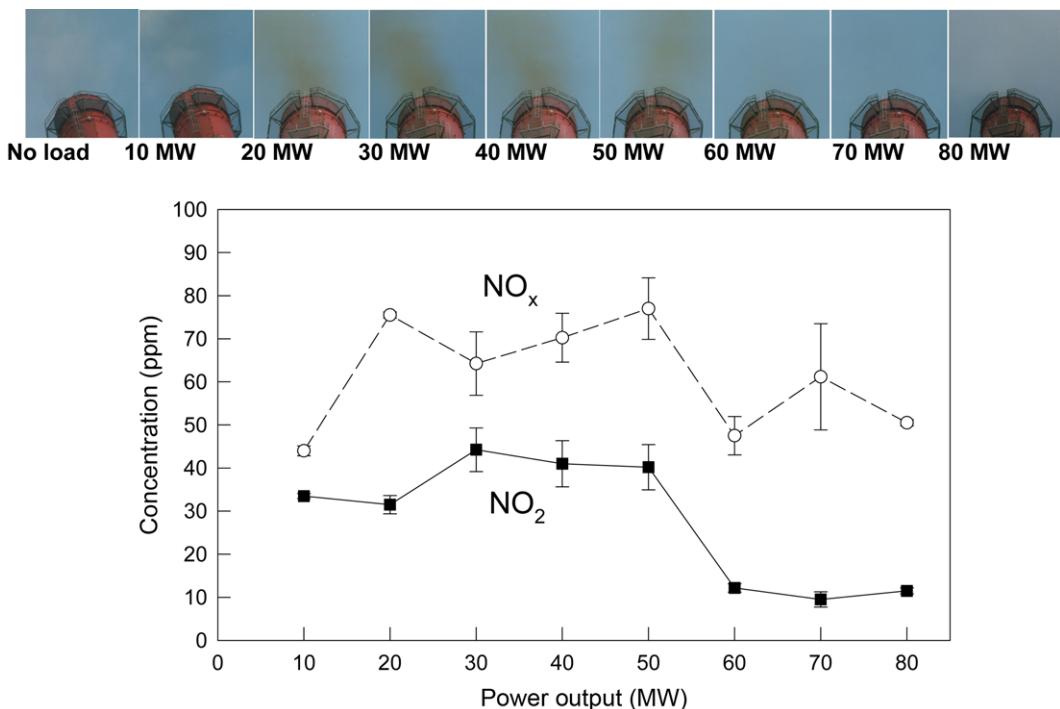
**Fig. 3.** Change in NO<sub>2</sub> conversion over 0.25 wt% Pt catalyst as a function of reactor inlet temperature when using four different reducing agents (GHSV 12,500 h<sup>-1</sup>, inlet gas composition: NO<sub>2</sub> 120 ppm, NO 20 ppm, O<sub>2</sub> 16%, CO<sub>2</sub> 2.5%, H<sub>2</sub>O 5%, N<sub>2</sub> balance).

30 ppm of NO<sub>2</sub> in the exhaust gas is the main reason for the yellow plume phenomenon (the diameter of the stack was 500 cm).

It should be pointed out that the total NO<sub>x</sub> concentration of the exit stream from the above gas-fired power plant is below 80 ppm at any stage of the operation, which is far lower than the current limit of Korean regulation (400 ppm). However, the visible yellow plume observed during daily start-up and shutdown periods of the gas-fired power plants irritates nearby residents and causes numerous petitions for corrective actions.

### 2. Effects of Reducing Agent

The temperature programmed reaction of NO<sub>2</sub> reduction was carried out in a small-scale reactor over the 0.25 wt% Pt impregnated catalyst using different reducing agents, and the results are shown



**Fig. 2.** Change in the color, NO<sub>2</sub> and NO<sub>x</sub> concentration of exhaust gas from the stack during the start-up period of a gas turbine.

in Fig. 3. The rate of the liquid reducing agent added to the stream was determined in such a way that the mole ratio of carbon atoms in the reductant to  $\text{NO}_2$  was 8. For example, diesel oil was regarded as hexadecane and the mole ratio of diesel oil to  $\text{NO}_2$  was 0.5. However, in the case of CO, the  $\text{CO}/\text{NO}_2$  ratio was 2.76.

As can be seen in Fig. 3, more than 90% of  $\text{NO}_2$  reduction was obtained at temperatures as low as 70 °C with methanol or CO reductants. When ethanol was used as the reducing agent, the active temperature window for the  $\text{NO}_2$  conversion higher than 90% was around 110 °C. In the case of the diesel oil reductant, the active temperature window was even higher (130–170 °C). The results in Fig. 3 indicate that the active temperature window of maximum  $\text{NO}_2$  reduction can be varied over the same catalyst by changing the reducing agent. It should be pointed out that  $\text{NO}_2$  was converted to NO not to  $\text{N}_2$  in all of the runs shown in Fig. 3. In other words, the summation of NO and  $\text{NO}_2$  concentration at the outlet of the reactor was the same as the summation of the inlet  $\text{NO}_x$  (NO and  $\text{NO}_2$ ) concentration, indicating that no reduction of  $\text{NO}_2$  further than NO was taken place. However, even with reduction of  $\text{NO}_2$  only to NO, decolorization of yellow plume can be achieved.

Catalytic reduction of NO in an oxygen-rich environment using the CO reducing agent over Pt catalysts was recently studied. Macleod and Lambert [14] tested the  $\text{NO}_x$  reduction activity of a 0.5 wt%  $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$  catalyst with 4,000 ppm of CO for the feed gas containing 500 ppm NO and 5%  $\text{O}_2$ . They reported similar results to ours in that they were not able to observe any  $\text{NO}_x$  reduction below 200 °C but only about the 10%  $\text{NO}_x$  conversion at 250 °C. Instead of NO reduction, NO oxidation to  $\text{NO}_2$  started to take place from 230 °C. In a separate experiment, CO was completely oxidized at that temperature and there must have been no reducing agent to prevent NO oxidation to  $\text{NO}_2$ . They might have observed  $\text{NO}_2$  reduction to NO at temperatures lower than 200 °C, if the feed gas contained  $\text{NO}_2$ .

At those temperatures of the high  $\text{NO}_2$  conversion shown in Fig. 3, most of the excess amounts of reducing agents were also oxidized over the same catalyst. Fig. 4 shows the conversion of CO during  $\text{NO}_2$  reduction. Although the amount of CO introduced to the gas stream was 2.76 times larger than  $\text{NO}_2$  in mole basis, more than 80% of total CO was converted to  $\text{CO}_2$  at the high end of the temperature window (100 °C). When the  $\text{NO}_2$  conversion started

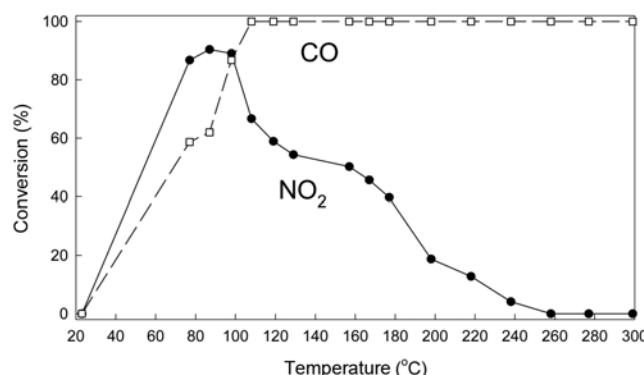


Fig. 4. Change in  $\text{NO}_2$  and CO conversion over 0.25 wt% Pt catalyst as a function of reactor inlet temperature (GHSV 12,500  $\text{h}^{-1}$ , inlet gas composition:  $\text{NO}_2$  120 ppm, NO 20 ppm,  $\text{O}_2$  16%,  $\text{CO}_2$  2.5%,  $\text{H}_2\text{O}$  5%, CO 600 ppm,  $\text{N}_2$  balance).

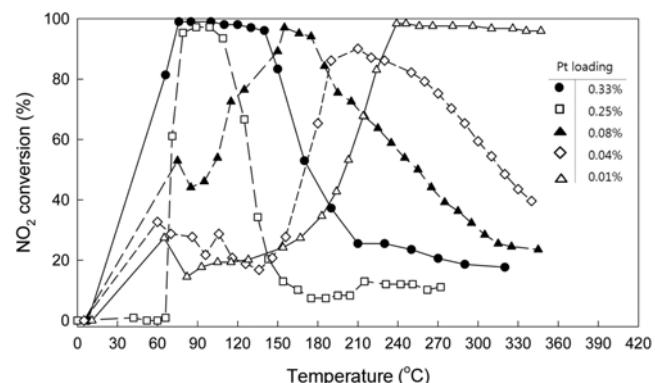


Fig. 5. Change in  $\text{NO}_2$  conversion over alumina supported Pt catalysts with different Pt loading as a function of reactor inlet temperature when using methanol reductant (GHSV 12,500  $\text{h}^{-1}$ , inlet gas composition:  $\text{NO}_2$  120 ppm, NO 20 ppm,  $\text{O}_2$  16%,  $\text{CO}_2$  2.5%,  $\text{H}_2\text{O}$  5%,  $\text{N}_2$  balance, methanol/ $\text{NO}_2$ =8).

to decrease, the CO conversion was complete. At those temperatures the normal CO oxidation activity of the Pt catalyst seemed to be higher than the  $\text{NO}_2$  reduction activity by CO.

### 3. Effects of Pt Loading

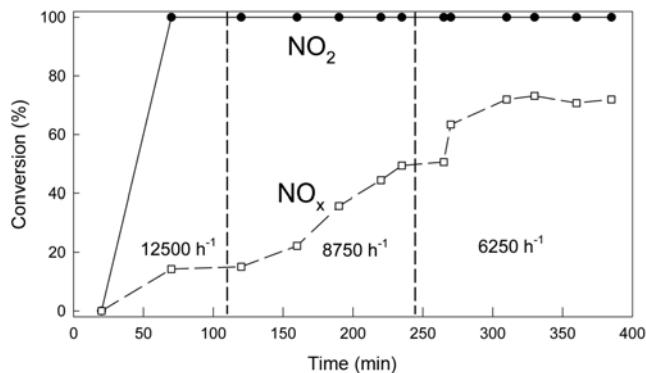
Five alumina washcoated catalysts with different Pt loading were prepared, and their catalytic activities toward the  $\text{NO}_2$  reduction with the methanol reducing agent are shown in Fig. 5. Pt loading was varied between 0.01 wt% and 0.33 wt% based on the total weight of the catalyst including the monolith. As can be seen, the catalyst with higher Pt loading shows the window of high  $\text{NO}_2$  reduction at lower temperatures. The catalyst loaded with 0.33 wt% Pt converted more than 95% of  $\text{NO}_2$  at temperatures as low as 70 °C. The temperature window of that catalyst for more than 90% of  $\text{NO}_2$  conversion spans to 140 °C. However, the temperature window for  $\text{NO}_2$  conversion higher than 90% for the catalyst with 0.08 wt% Pt was between 150 and 180 °C. The 0.01 wt% Pt catalyst was active for  $\text{NO}_2$  reduction at temperatures higher than 240 °C. Fig. 5 clearly shows that the temperature window for high  $\text{NO}_2$  conversion can be varied by changing the catalyst composition, especially the Pt loading.

The above result of changing the active temperature window of  $\text{NO}_2$  conversion by using a different composition catalyst has practical importance. The  $\text{NO}_2$  decolorization process utilizing the combination of Pt catalysts and the reducing agents above can be applied directly to the exhaust gases discharging at temperatures between 70 °C to 360 °C, making it unnecessary to install additional heating/cooling devices.

Change in the activities of the catalysts with different metal loading is frequently observed when the reaction is structure-sensitive. CO oxidation over supported gold catalysts is a good example. The higher loading catalyst normally contains more metal particles with the larger size [15]. Thus,  $\text{NO}_2$  reduction to NO over a Pt catalyst seems to be a structure-sensitive reaction with larger Pt particles being more active at lower temperatures.

### 4. Effects of Space Velocity

The flow rate of the simulated gas entering the reactor was varied while the temperature was maintained at 100 °C. The methanol injection rate was also changed to make the methanol/ $\text{NO}_2$  ratio remain constant at 8. As shown in Fig. 6, the concentration of  $\text{NO}_x$  ( $\text{NO}+$



**Fig. 6.** Change in NO<sub>2</sub> and NO<sub>x</sub> conversion over 0.33 wt% Pt catalyst at different space velocities (100 °C, inlet gas composition: NO<sub>2</sub> 120 ppm, NO 20 ppm, O<sub>2</sub> 16%, CO<sub>2</sub> 2.5%, H<sub>2</sub>O 5%, N<sub>2</sub> balance, methanol/NO<sub>2</sub>=8).

NO<sub>2</sub>) decreased at the exit of the reactor as the space velocity was lowered, while maintaining the 100% of NO<sub>2</sub> conversion. The result shown in Fig. 6 suggests that the combination of the 0.33 wt% Pt catalyst and the methanol reductant was able to obtain the reduction product of NO<sub>2</sub> other than NO at lower space velocities. Our gas analyzer was not equipped with an N<sub>2</sub>O measurement sensor. Thus, it is not clear what portion of NO<sub>2</sub> was converted N<sub>2</sub>. However, it should be pointed out that more than 60% of NO<sub>2</sub> reduction further than NO at 100 °C with the space velocity of about 6,000 h<sup>-1</sup> is possible with the combination of the Pt catalyst and the methanol reducing agent.

### 5. Pilot-scale Test

The first set of catalysts tested in the pilot-scale unit was composed of four 1,125 cm<sup>3</sup>-sized honeycomb type catalysts with the cell density of 200 cpi (dimension: 15 cm×15 cm×5 cm). Total volume of the catalyst was 4,500 cm<sup>3</sup>. The Pt loading on alumina washcoat was 0.22% based on the total weight of the catalyst. The gas turbine power output was adjusted at 40 MW (a half of full power output) and the exhaust gas from the stack showed a yellow color. The composition of the gas turbine exhaust gas diverted to enter the decolorization reactor was 14 ppm of NO, 22 ppm of NO<sub>2</sub>, 470 ppm of CO, 2% of CO<sub>2</sub>, 18% of O<sub>2</sub>, 4% of H<sub>2</sub>O (estimated) with N<sub>2</sub> balance. The temperature of the inlet gas without heating was between 120 °C and 130 °C. In some cases, the regulated electricity was ap-

plied to the electrical heater so that the inlet gas temperature was increased up to 249 °C. The NO<sub>2</sub> reduction test was carried out with or without the methanol addition. The rate of methanol injection was 3 cm<sup>3</sup>/min, which corresponds to the molar ratio of methanol/NO<sub>2</sub> to be 14.5 and 11.1 for the GHSV of 70,000 h<sup>-1</sup> and 92,000 h<sup>-1</sup>, respectively. In the case of no methanol injection, the inherent CO in the exhaust gas acted as the reductant. Table 1 lists the NO<sub>2</sub> reduction performance of the 0.22 wt% Pt catalyst.

At the exhaust gas temperature of 127 °C, 77% of NO<sub>2</sub> was converted to NO even without the methanol injection. At the same time, 23% of CO was converted to CO<sub>2</sub>, indicating CO was acting as the reductant. When methanol was added to the gas stream at 122 °C, the NO<sub>2</sub> conversion was 64%. In this case a portion of NO<sub>2</sub> was reduced further than NO. However, the CO conversion was only 9.4%, suggesting that methanol oxidation and CO oxidation share the same catalytic sites. It is expected from the lab-scale test that the 0.22 wt% Pt catalyst can reduce NO<sub>2</sub> much more than 70% at temperatures of about 120 °C (Fig. 5). However, considering 5.7 times larger space velocity of the pilot test than that of the lab-scale run, only 64 to 77% of NO<sub>2</sub> conversion at temperatures of about 120 °C can be attributed to high space velocities.

As the inlet gas temperature was increased to 220 °C or higher, the NO<sub>2</sub> conversion became larger than 95% and the outlet gas stream contained NO<sub>2</sub> less than or equal to 1 ppm. At the same time, the CO conversion was also increased from 69.4% at 220 °C to 92.3% at 240 °C. Especially at 249 °C, CO present in the gas stream was able to reduce NO<sub>2</sub> to completely NO, indicating that the injection of the methanol reductant was not necessary to reduce NO<sub>2</sub> if there was enough CO in the exhaust gas.

Another set of the pilot-scale experiment was carried out with a higher loading Pt catalyst, intending to achieve the high NO<sub>2</sub> conversion at the gas turbine exhaust temperature of about 120 °C. The second set of the catalyst was prepared by the Korean catalyst manufacturer (General System Co.). The amount of alumina washcoated was 20% of the weight of the ceramic monolith (400 cpi, dimension: 15 cm×15 cm×10 cm). Platinum loading was 0.27% of the total weight of the catalyst. The volume of totally four pieces of the catalyst was 9,000 cm<sup>3</sup>. Again, the gas turbine's power output was set at 40 MW and the composition of the exhaust gas for this run was 14-15 ppm of NO, 21-27 ppm of NO<sub>2</sub>, 445-460 ppm of CO, 2.6% of CO<sub>2</sub>, 18% of O<sub>2</sub>, 5% of H<sub>2</sub>O (estimated) and with N<sub>2</sub> balance. The temperature of the inlet gas was between 102 and 124 °C.

**Table 1.** Change in NO<sub>2</sub>, NO<sub>x</sub> and CO concentration over 0.22 wt% Pt catalyst with or without methanol injection (catalyst volume: 4,500 cm<sup>3</sup>)

Temperature (°C)	Inlet	127	122	220	230	235	240	249
Space velocity (h <sup>-1</sup> )		70,000	70,000	92,000	92,000	92,000	92,000	92,000
Methanol (cm <sup>3</sup> /min)		0	3	3	3	3	3	0
NO (ppm)	14	33	16	36	35	36	36	33
NO <sub>2</sub> (ppm)	22	5	8	1	1	0	0	0
NO <sub>x</sub> (ppm)	36	38	24	37	36	36	36	33
CO (ppm)	470	363	426	144	100	52	36	41
NO <sub>2</sub> conversion (%)		77.3	63.6	95.5	95.5	100	100	100
NO <sub>x</sub> conversion (%)		-5.6	33.3	0	0	0	0	8.3
CO conversion (%)		22.7	9.4	69.4	78.7	88.9	92.3	91.3

**Table 2. Change in NO<sub>2</sub>, NO<sub>x</sub> and CO conversion over 0.27 wt% Pt catalyst at different space velocities (catalyst volume: 9,000 cm<sup>3</sup>)**

Space velocity (h <sup>-1</sup> )	28,000	60,000	95,000
Temperature (°C)	102	117	123
NO <sub>2</sub> conversion (%)	96	96	96
NO <sub>x</sub> conversion (%)	0	0	0
CO conversion (%)	87	84	71

**Table 3. Change in NO<sub>2</sub> and CO conversion over 0.27 wt% Pt catalyst at different inlet temperatures (space velocity: 28,000 h<sup>-1</sup> and catalyst volume: 9,000 cm<sup>3</sup>)**

Temperature (°C)	102	116	148	175	192
NO <sub>2</sub> conversion (%)	96	96	96	92	88
CO conversion (%)	87	85	92	95	96

No additional reductant was injected.

Table 2 lists results of NO<sub>2</sub> reduction over the 0.27 wt% Pt catalyst with varying space velocities at the exhaust gas temperatures of 102 °C to 123 °C. In this experiment the concentrations of NO<sub>2</sub> and CO fluctuated to a certain degree. Thus, each conversion was calculated based on the difference between the inlet gas concentration and the reactor exit concentration at the time of the measurement. As shown in Table 2, more than 95% of NO<sub>2</sub> is reduced over all the space velocities tested ranging between 28,000 h<sup>-1</sup> and 95,000 h<sup>-1</sup>. The concentration of NO<sub>2</sub> at the exit of the reactor was 1 ppm in all cases. A space velocity higher than 95,000 h<sup>-1</sup> was not able to be obtained because the capacity of the blower was limited to supply the maximum gas flow rate of 853 m<sup>3</sup>/hr. Again, the conversion of NO<sub>x</sub> being zero means that all of NO<sub>2</sub> was converted to NO. Meanwhile, CO conversion decreased as the space velocity increased, suggesting that the CO oxidation activity of the catalyst is not high enough at those temperatures.

The effect of the inlet gas temperature on the NO<sub>2</sub> and CO conversion can be found in Table 3. Similar to the behavior of the 0.33 wt% Pt catalyst at the lab-scale unit shown in Fig. 5, the NO<sub>2</sub> conversion started to decrease at temperatures higher than 175 °C over the 0.27% Pt catalyst at the pilot-scale test. Again, oxidation of CO was almost complete at those temperatures and oxidation of NO to NO<sub>2</sub> seemed to take place.

## CONCLUSION

The catalytic NO<sub>2</sub> reduction process of the present study was very effective in decolorizing yellow-colored exhaust gases containing NO<sub>2</sub> at a wide range of temperatures from 70 °C to 360 °C, by just employing Pt catalysts with the different composition and the inher-

ent CO in the exhaust gas. Its effectiveness was verified in a pilot-scale test utilizing the real gas turbine exhaust gas with 96% conversion of NO<sub>2</sub> at the exhaust gas temperature of about 110 °C. For the sole purpose of decolorization, the present process has advantages over conventional SCR or NSCR processes in that it operates at exhaust gas temperatures obviating additional heating/cooling devices and the corresponding operating costs. Moreover, the process can be operated with hydrocarbon or alcohol reducing agents. Although expensive platinum is used as the catalyst, more than 96% conversion of NO<sub>2</sub> at the space velocity of 95,000 h<sup>-1</sup> requires a smaller amount of the catalyst. NO<sub>2</sub> was reduced only to NO at space velocities higher than 12,500 h<sup>-1</sup>. However, there is a potential that this catalytic process can reduce NO<sub>2</sub> further than NO at lower space velocities and at temperatures as low as 100 °C.

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## REFERENCES

1. A. S. Feitelberg and S. M. J. Correa, *Eng. Gas Turbines and Power*, **122**, 287 (2000).
2. J. A. Miller and C. T. Bowman, *Prog. Energy Combust. Sci.*, **15**, 287 (1989).
3. J. W. Hunderup and R. J. Roby, *Transactions of the ASME*, **118**, 756 (1996).
4. R. A. Searles, *Chemistry and Industry*, **16**, 895 (1974).
5. R. D. Bell, US Patent, 5,022,226 (1991).
6. Y. Cai and U. S. Ozkan, *Appl. Catal.*, **78**, 241 (1991).
7. M. Wallin, C. J. Karlsson, M. Skoglundh and A. Palmqvist, *J. Catal.*, **218**, 354 (2003).
8. R. Burch, J. P. Breen and F. C. Meunier, *Appl. Catal. B: Environmental*, **39**, 283 (2002).
9. A. B. Mhadeshwar, B. H. Winkler, B. Eiteneer and D. Hancu, *Appl. Catal. B: Environ.*, **89**, 229 (2009).
10. O. Okada, T. Tabata, M. Kokitsu, H. Ohtsuka, L. M. F. Sabatino and G. Bellussi, *Appl. Surf. Sci.*, **121/122**, 267 (1997).
11. Y. Traa, B. Burger and J. Weitkamp, *Micropor. Mesopor. Mater.*, **30**, 3 (1999).
12. A. Subbiah, B. K. Cho, R. J. Blint, A. Gujar, G. L. Price and J. E. Yie, *Appl. Catal. B: Environ.*, **42**, 155 (2003).
13. H. He and Y. Yu, *Catal. Today*, **100**, 37 (2005).
14. N. Macleod and R. M. Lambert, *Appl. Catal. B: Environ.*, **35**, 269 (2002).
15. A. Wolf and F. Schuth, *Appl. Catal. A: Gen.*, **226**, 1 (2002).