ELSEVIER

Catalysis Today 29 (1996) 109–115

CATALYSIS TODAY

The state-of-the-art technology of NO_x control

Fumito Nakajima *, Ikuhisa Hamada

Kure Research Laboratory, Babcock-Hitachi K.K., Takara-machi, Kure-shi, Hiroshima-ken 737, Japan

Abstract

The TiO_2-based DeNOx catalyst which is now commercially implemented world-wide is described, emphasizing the importance of the resistance to SO_x-poisoning and plugging by particulates. Various NO_x reduction technologies are compared and recent trends in catalytic DeNOx installations in Japan are reviewed. For wider applications and to meet the stringent emission requirements, newly developed DeNOx catalysts such as for high-temperature gas turbine exhaust and for simultaneous removal of NO_x and CO are also introduced.

Keywords: NO_x control; $DeNO_x$

1. Introduction

Innovation in industrial catalysis has always been derived from the strong social and industrial needs. Because of the urgent requirements for ammonia in the manufacturing of explosives in Germany during World War I, the first breakthrough in ammonia synthesis with the iron oxide catalyst was resulted from the work of Haber and Bosch. Similarly, the TiO_2-based catalyst for NO_x removal was invented by the author and his colleagues in 1973, in response to the urgent needs to mitigate air pollution, especially photochemical smog in urban and industrial area of Japan.

Both combustion control and post-combustion flue gas treatment are currently available for the reduction of NO_x emission from stationary combustion sources. With the combustion control and the low NO_x burner, the NO_x emission can be reduced to 100 or 200 ppm. In order to meet the strict emission standard, the flue gas treatment is required. Among many proposed methods, the catalytic NO_x removal process has been found most feasible and the selective catalytic reduction (SCR) with ammonia is widely implemented to the utility boilers and other industrial combustion facilities.

Commercial application of the catalytic $DeNO_x$ has been initiated in Japan since 1977, four years from our invention of the TiO_2-based catalyst. It is recognized that the industrial success of the catalytic removal of NO_x could not be realized without the invention of the TiO_2-based catalyst. The TiO_2-based catalyst predominates in SCR $DeNO_x$ process as the iron oxide catalyst in ammonia synthesis.

2. Invention of the TiO_2-based catalyst

A key element of the catalytic $DeNO_x$ system is a 'high performance' catalyst. Several hun-

---

* Corresponding author.

SSDI 0920-5861(95)00288-X

Table 1
Properties of the typical DeNO$_x$ catalysts

Catalyst	TiO_2-type	Fe_2O_3-type	Al_2O_3-type
Catalytic activity	High	Medium	Low
Resistance to SO$_x$	High	Low [a]	Low [b]
Selectivity	High	Low (> 450°C)	Low (> 450°C)
Oxidation of SO_2 to SO_3	Low	High	High
Regeneration [c]	Possible	Impossible	Impossible

[a] Formation of $Fe_2(SO_4)_3$.
[b] Formation of $Al_2(SO_4)_3$.
[c] Removal of deposited NH_4HSO_4 by heating above 300°C.

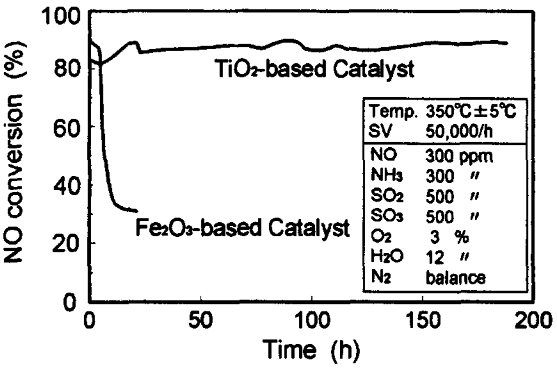

Fig. 1. SO$_x$ poisoning test.

dreds of catalysts were examined in the early stage of catalyst development. The catalysts studied are classified as shown in Table 1. Metal oxide catalysts, such as Fe_2O_3, Fe_2O_3–Cr_2O_3, Fe_2O_3–WO_3, Fe_2O_3 supported on Al_2O_3 and V_2O_5 supported on Al_2O_3 were proved to have a high activity for NO–NH_3 reaction in the presence of a large excess of oxygen. These catalysts, however, lose their activity easily in a few hundred hours due to SO$_x$ poisoning. The catalyst components such as Fe_2O_3 and Al_2O_3 easily react with SO$_x$ to form their sulfates at operating temperatures, i.e., 200–400°C. A drastic decrease of pore volume and surface area of the catalysts was observed with the formation of sulfates. As a result of extensive exploratory studies of catalysts, it was found that TiO_2 does not react with SO$_x$ and shows a high activity for NO–NH_3 reaction. The SO$_x$ poisoning test indicates a high stability of the TiO_2-based catalysts as shown in Fig. 1. The experiments were performed with a test gas containing 500 ppm SO_3 using either a WO_3 (15 wt.-%)–Fe_2O_3 (85 wt.-%) catalyst or a WO_3 (10 wt.-%)–TiO_2 (90 wt.-%) catalyst. Fig. 1 indicates that the catalyst composed mainly of Fe_2O_3 lose its activity very rapidly. On the other hand, the WO_3–TiO_2 catalyst, composed mainly of TiO_2, maintained the initial activity for 200 h. The most outstanding issue of this invention is that the TiO_2-based catalysts exhibit resistance to SO$_x$ poisoning over a wide range of temperatures, 200–600°C. TiO_2 essentially reacts with neither SO_3 nor SO_2 at temperatures above 200°C and, therefore, is able to keep its structure over a long period of exposure to SO$_x$-containing flue gases.

Patents disclose the TiO_2-based catalysts for selective catalytic reduction of NO$_x$ with NH_3 [1,2]. Second components of the TiO_2-based catalysts are selected from a group of V_2O_5, MoO_2, WO_3, Fe_2O_3, CoO, NiO, MnO_2, Cr_2O_3, CuO, U_3O_8 and so on. The TiO_2-based catalysts show high activity and selectivity for the reaction between NO and NH_3 in the presence of large excess of oxygen, at a temperature range of 200 to 500°C, as shown in Fig. 2. TiO_2 plays a role, not only as a catalyst support, but also as a promoter of the catalytic reaction.

It is known that NO$_x$ is selectively reduced by NH_3 in the presence of a large excess of O_2.

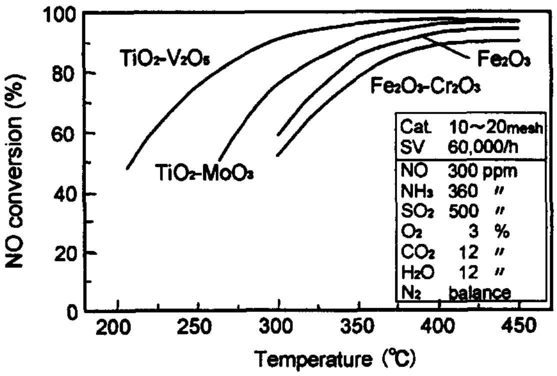

Fig. 2. Catalytic activity of various catalysts on NO–NH_3 reaction.

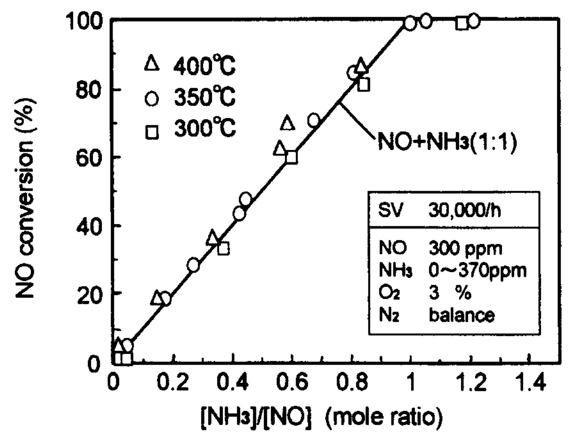

Fig. 3. NO conversion as a function of $[NH_3]/[NO]$ ratio — Effect of temperature.

The reaction stoichiometry is elucidated as follows [3]:

$$NO + NH_3 + \tfrac{1}{4}O_2 = N_2 + \tfrac{3}{2}H_2O \qquad (1)$$

A careful experiment was carried out in order to determine the reaction stoichiometry of NO_x and NH_3. Fig. 3 shows the NO conversion as a function of NH_3/NO ratio at varied temperatures. The reaction proceeds in one to one molar ratio of NH_3 to NO. Co-existence of excess oxygen is necessary to enhance the $NO–NH_3$ reaction.

In the $NO_2–NH_3$ system, the overall reaction is given as

$$3NO_2 + 4NH_3 = \tfrac{7}{2}N_2 + 6H_2O \qquad (2)$$

No effect of co-existence of oxygen is observed for the $NO_2–NH_3$ reaction.

In the $NO–NO_2–NH_3$ system, the overall reaction is given as,

$$NO + NO_2 + 2NH_3 = 2N_2 + 3H_2O \qquad (3)$$

The reaction of equimolar $NO–NO_2$ with NH_3 is the fastest among three reactions. When both NO and NO_2 are contained in the flue gas, the reaction between equimolar $NO–NO_2$ and NH_3 proceeds first and the reaction of remaining NO or NO_2 follows.

The most part of NO_x in the actual combustion flue gases is contained as NO and NO_2 is less than one tenth of NO. In the industrial $DeNO_x$ practice, therefore, NH_3 addition to the flue gas has to be controlled based on the one-to-one ratio of the $DeNO_x$ reaction.

3. Commercial implementation

A typical flue gas treatment for a boiler is shown in Fig. 4. The flue gas from a boiler economizer at a temperature of 300 to 400°C is mixed with NH_3 and introduced into the NO_x removal catalyst reactor, where NO_x is reduced to N_2 and H_2O by reacting with NH_3 and O_2. The flue gas is then heat-exchanged in an air heater. An electrostatic precipitator for dust removal and a desulfurization unit, if necessary, are installed downstream of the $DeNO_x$ reactor. Fig. 5 shows an example of the catalytic $DeNO_x$ reactor.

A few important points encountered at the stage of the commercial implementation of the catalytic $DeNO_x$ should be mentioned. Since the volume of flue gas to be treated is extraordinarily large, for example, 2000000 $Nm^3\ h^{-1}$ for 700 MW fossil fueled power plant and contains various amounts of particulates, it is important to minimize pressure loss across the catalyst bed and to prevent plugging with the particulates. A fixed bed reactor with tablet- or granular-type catalyst is apt to be plugged with particulate matters. Parallel-flow reactor is the most effective and reliable choice to prevent plugging. Two types of the parallel-flow catalyst, plate-type and honeycomb monolith-type, are widely employed. Pictures of the catalyst units are shown in Fig. 6. Catalyst plate elements having notches are arranged and packed in the catalyst unit, the size of which is 500 × 500 × 500 mm. The extruded element of the honeycomb-type

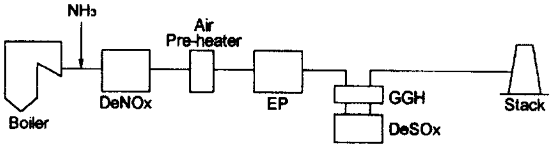

Fig. 4. Typical flue gas treatment system with $DeNO_x$ unit.

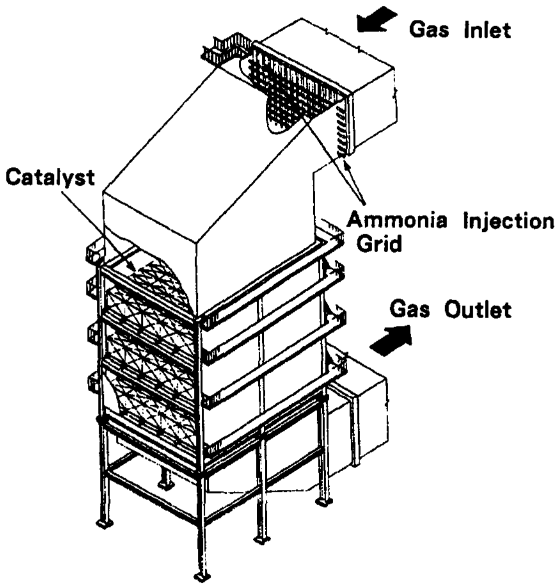

Fig. 5. Conventional boiler application of DeNO$_x$ unit.

catalyst is about 150 × 150 × 500 mm. Catalysts with various plate separations or channel dimensions from 4 to 10 mm are selected for each specified application. Different dimensions give the difference in the specific geometric area of catalyst. A wider separation is applied for coal-fired flue gas which contains higher concentration of particulates. Since a pressure loss is much lower for the plate-type catalyst, a high gas linear velocity is allowed.

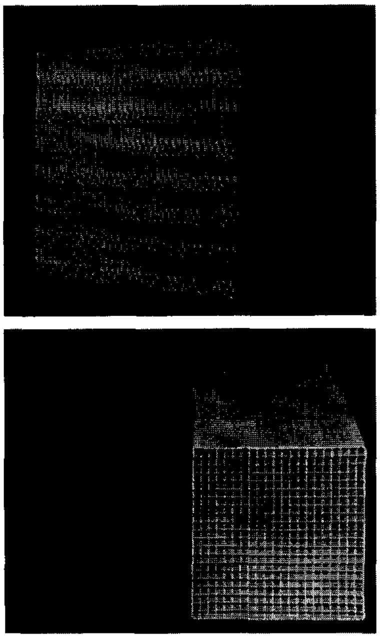

Fig. 6. Parallel flow catalysts.

It is also important to control ammonia injection to the flue gas in order to obtain the highest removal of NO$_x$ and to minimize excess ammonia slip. As mentioned before, the reaction proceeds in one to one molar ratio of NH_3 to NO$_x$. The fundamental control philosophy is to provide ammonia injection at a constant NH_3/NO_x molar ratio. The NH_3/NO_x ratio at the inlet of the reactor must be kept in the range of just below stoichiometry.

There are some problems encountered in an operation of a practical DeNO$_x$ plant with a boiler flue gas. Deposition of ammonium hydrogen sulfate in the catalyst pores is observed at a temperature below 200°C. The temperature in a steady state of operation must be kept above 220°C for the SO$_x$ containing flue gases. The higher the operating temperature becomes, i.e., above 400°C, the higher conversion of SO_2 to SO_3 are observed. Since V_2O_5 promotes the SO_2 oxidation, the TiO_2–MoO_3 or TiO_2–WO_3 catalyst is used with minimization or elimination of V_2O_5 in the catalyst ingredients. Most of the commercial catalytic DeNO$_x$ units are applied at a gas temperature of 300 to 400°C, which generally meets the temperature of the boiler flue gas at the exit of the economizer section. A stable and satisfactory operation of the commercial catalytic DeNO$_x$ has been performed for a long period without any problems caused by deposition of ammonium hydrogen sulfate in the catalyst or in the downstream equipment.

Various control technologies for NO$_x$ reduction and their applications to fossil fueled powder station are summarized in Table 2. Combustion modifications, such as two stage combustion, flue gas recirculation, low NO$_x$ burner and in-furnace NO$_x$ reduction, have been commercially applied in Japan since early 1970s.

These control technologies have demonstrated 30% to 60% reduction of NO$_x$ in both

Table 2
Application of NO_x control to fossil fueled power stations

NO_x control technology	Fuel	NO_x level (ppm)	Start of commercial application
(1) Two stage combustion, Flue gas recirculation	Gas	ca. 55–110	1972
	Oil	ca. 95–180	1972
	Coal	ca. 300–350	1972
(2) (1) + Low NO_x burner	Gas	ca. 40–100	1975
	Oil	ca. 85–180	1974
	Coal	ca. 160–300	1975
(3) In-furnace NO_x reduction	Gas	ca. 40–60	1985
	Oil	ca. 50–85	1981
(4) Catalytic $DeNO_x$	Gas	ca. 10–20	1977
	Oil	ca. 20–30	1977
	Coal	ca. 50–80	1980

new and existing boiler plants. However, we need to add the catalytic $DeNO_x$ units to the combustion modifications, because the emission regulation for NO_x is very strict to the utility boilers and combined cycle plants. Commercial implementations of the catalytic $DeNO_x$ started in 1977 and have expanded rapidly especially in Japan.

According to the survey of the Environmental Agency of Japan, the cumulative number of the installations of NO_x control in Japan amounts to 826 units in 1993 as shown in Fig. 7. The number of installations for various industries is as follows. Utility industry: 173 units (20.9%); waste incineration: 139 units (16.8%); chemical industry: 99 units (12.0%). Total capacity of the installations is estimated to be 243 million m^3 per h of the flue gas treated. Main contributor is the utility industry. Capacity of the flue gas from utility power plants, of which NO_x emission is controlled, amounts to 196 million m^3 per h and accounts for 80% of the total capacity. Although the number of $DeNO_x$ is less than a half of than that of $DeSO_x$, the total gas volume of capacity of $DeNO_x$ exceeds that of $DeSO_x$.

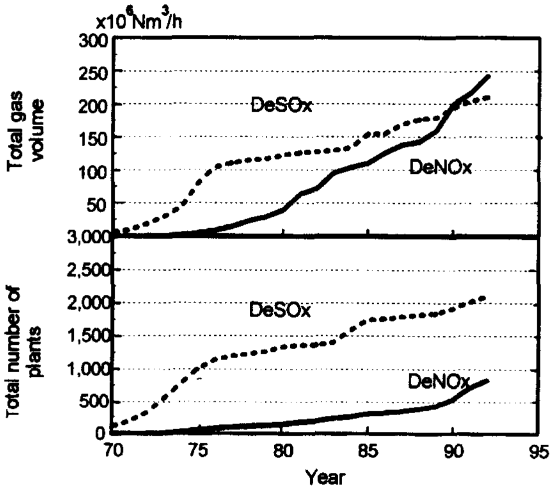

Fig. 7. Commercial installations of $DeNO_x$ and $DeSO_x$ in Japan.

All utility companies in Japan have introduced the catalytic $DeNO_x$ and more than 100 units are fitted to the utility boilers and combined cycle plants. Total capacity fitted with the catalytic $DeNO_x$ units is more than 50000 MW which corresponds to 50% of the fossil-fueled power generation of Japan. Japanese utility companies are required compulsively to equip their new fossil-fueled power plants with the catalytic $DeNO_x$ units.

4. New development of catalytic $DeNO_x$

It is clear that the catalytic $DeNO_x$ process using the TiO_2-based catalyst is a well established technology. Further developments should be considered here.

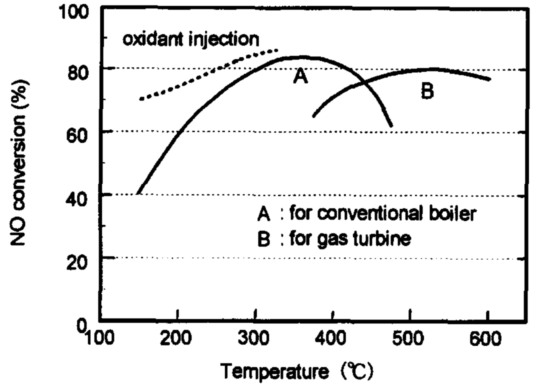

Fig. 8. High and low temperature applications of catalytic DeNO$_x$.

1. Extended applications to high and low temperatures.
2. High efficiency of NO$_x$ removal (more than 90%).
3. Simultaneous removal of CO and NO$_x$.
4. SCR with urea or other N compounds.
5. SCR with hydrocarbon.
6. Direct decomposition.
7. Simultaneous removal of NO$_x$ and SO$_x$.

Gas turbines and some industrial furnaces require high temperature applications for the catalytic DeNO$_x$ with ammonia. The most extensive applied catalyst is used at temperatures from 300 to 400°C. In Fig. 8, the performance of new catalyst (B) for high temperature applications is shown in comparison to the conventional one (A). The new catalyst consists of TiO_2–WO_3 and exhibits high activity and thermal stability at the temperatures from 450 to 600°C. The high temperature catalyst is applicable to the exhaust from industrial gas turbines, the temperature of which is usually 550 to 600°C. Several commercial DeNO$_x$ units for the industrial gas turbine are operating satisfactorily.

For the low temperature applications, we proposed an oxidant or NO_2 injection to the combustion flue gas in addition to the ammonia injection. If we could prepare equimolar NO–NO_2 in the flue gas, the NH_3–NO_x reaction would be strikingly accelerated even at a temperature below 200°C. It is expected to obtain a high efficiency of NO$_x$ removal for low temperature applications without heating up to above 300°C and consequently to save energy consumption in the catalytic DeNO$_x$ system.

Stoichiometry of NO$_x$ reduction is a one to one molar ratio of NH_3 to NO$_x$. In order to minimize excess NH_3 slip, the operating molar ratio is kept to less than 1.0; for example 0.8 to 0.9. If the excess NH_3 slip is not allowed, it is difficult to attain more than 90% removal. A new catalyst, which has an activity to decompose excess NH_3 to nitrogen and water as well as to promote NH_3–NO_x reaction in the presence of oxygen, was recently developed in our laboratory. Oxidation of NH_3 with NO$_x$ is followed by oxidation of NH_3 with oxygen on the new catalyst. More than 90% of NO$_x$ removal is achievable by using of the new catalyst and by keeping NH_3/NO_x ratio at a slightly higher than stoichiometry without a substantial increase of NH_3 slip.

Another recent development is a dual function catalyst, which exhibits high activity for not only NO$_x$ removal with ammonia but also CO oxidation. The original TiO_2-based catalyst has no activity for CO oxidation. It is well known that the precious metal catalyst is very active and widely employed for CO oxidation. With a combination of the TiO_2-based catalyst and precious metal, the dual function catalyst was obtained. The undesirable oxidation of am-

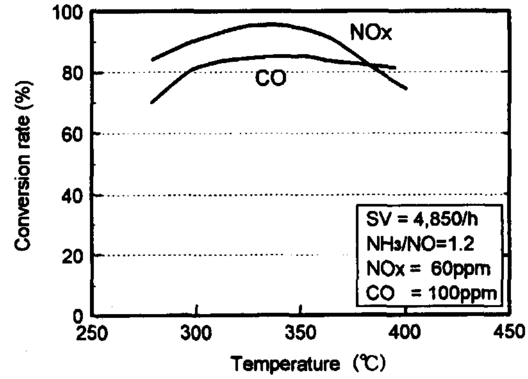

Fig. 9. Simultaneous removal of NO$_x$ and CO by dual-function catalyst.

monia is suppressed in this catalyst. The catalyst performance is shown in Fig. 9. The dual function catalyst is expected to be applied for simultaneous removal of CO and NO_x from the flue gas of combined cycle power plants.

The present process based on the SCR requires a liquid ammonia storage and distributing device. Because NH_3 is flammable and toxic, it is not preferable to use the device in the plants installed in a densely populated area. The use of aqueous ammonia solution is recommended instead of liquid ammonia. The other nitrogen compounds such as urea, melamine and cyanuric acid are found to give almost the same catalytic performance as ammonia. Aqueous solutions of these compounds are also commercially employed.

After the pioneering work by Iwamoto, much effort is devoted to using hydrocarbons as reductants for removal of NO_x from exhaust gases [4]. In spite of extensive studies, the performance of NO_x reduction with hydrocarbons is insufficient to bring it to commercial application in the stationary combustion sources. Direct decomposition of NO_x into its elements is the best technical solution and is certainly more desirable than adding a reductant to remove NO_x from flue gases. Although there are some challenging research works on catalytic decomposition of NO_x, they are still in the laboratory experimental phase.

In oil- and coal-firing boiler flue gases, oxides of both nitrogen and sulfur are present and simultaneous removal practice for NO_x and SO_x would be most acceptable. No such catalyst, however, is now known. Adsorption of SO_x coupled with SCR on charcoal is promising for the simultaneous removal with a limited application.

References

[1] F. Nakajima, M. Takeuchi, S. Matsuda, S. Uno, T. Mori, Y. Watanabe and N. Imanari, Jpn. Patent 1010563, 1034771, 1 115 421, 1 213 543 (appl. 1973), 141 763, 1 159 815, 1215760, 1 159918 (Appl. 1974).

[2] F. Nakajima, M. Takeuchi, S. Matsuda, S. Uno, T. Mori, Y. Watanabe and N. Imanari, US Patent 4085193, UK Patent 1495396, German Patent 2458888, Fr. Patent 7440992, Can. Patent 1 033 543, Indian Patent 1 027 634, S. Patent 154576/74, Korean Patent 7075.

[3] S. Matsuda, M. Takeuchi, T. Hishinuma, F. Nakajima, T. Narita, Y., Watanabe and M. Imanari, J. Air Pollut. Control Assoc., 28 (1978) 350, A. Kato, S. Matsuda, F. Nakajima, M. Imanari and Y. Watanabe, J. Phys. Chem., 85 (1981) 1710.

[4] M. Iwamoto (Editor), Catal. Today, 22 (1994) 1.