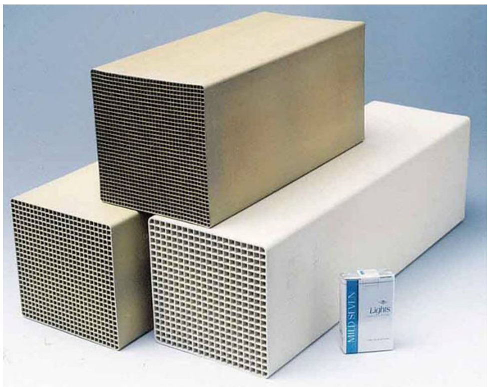
Technologies for Multifunctional De-NOx Catalyst and Recycling of Spent catalyst intended for Eco-Friendly Thermal Power Plants



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Emission control regulations have been tightened year after year throughout the world in response to increased desire for environmental conservation. To meet the new demands, more sophisticated flue gas cleaning technologies are needed that reduce nitrogen oxide (NOx) emissions, which cause acid rain and photochemical smog. Meanwhile, there is also increased interest in improved use of scarce resources through reduction of waste products and better recycling of rare metals. Mitsubishi Heavy Industries, Ltd. (MHI) has developed two unique catalysts for De-NOx used in thermal power plants and aims to respond quickly to the wide range of customer needs in the global market. The two types of catalyst are: (1) a catalyst intended for gas turbine power plants with high NO_2/NOx ratios and (2) a regenerated catalyst intended for coal-fired power plants.

1. Introduction

Operation of the first dry De-NOx system for boilers started in 1977, and it is estimated that more than 1,000 units are currently being used in commercial and industrial boilers as well as in gas turbines.[1]

MHI began development of De-NOx systems intended for boilers in 1974, and we have since been developing catalysts in response to the needs of customers and making efforts to improve reliability of the equipment. In the course of our development, we have delivered more than 500 De-NOx systems in Japan, mainly for use in commercial and industrial power plants. In addition, we have licensed our expertise to manufacturers in the United States and the European Union.[2]

In this paper, we present an overview of our recent De-NOx catalyst improvements and developments from the perspective of advanced technology for flue gas cleaning and rare metal recycling.

2. Improvement of Catalysts Intended for Gas Turbine Plants

The principal component of NOx (NO and NO_2) in combustion exhaust gas is NO. Therefore, the De-NOx reactions, in which NOx is reducted into nitrogen by NH_3, generally progress according to reaction (1) below. In cases where NO_2 coexists with NO, reactions (2) and (3) occur. If the percentage of NO_2 in NOx is less than 50%, NO_2 and NO are removed by reaction (2), and the NO that remains is removed by reaction (1). If the percentage of NO_2 in NOx is higher than 50%, however, NO_2 in the remaining NOx component system becomes rich in line as reaction (2) progresses. Under this circumstance, the De-NOx ratio drops because reaction (3) is slow, as shown in **Figure 1**.

$$4NO + 4NH_3 + O_2 \Rightarrow 4N_2 + 6H_2O \quad \cdots (1)$$
$$NO + NO_2 + 2NH_3 \Rightarrow 2N_2 + 3H_2O \quad \cdots (2)$$
$$6NO_2 + 8NH_3 \Rightarrow 7N_2 + 12H_2O \quad \cdots (3)$$

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In exhaust gas from gas turbines, the NO_2/NOx ratio tends to increase during startup and low load operation. The high NO_2/NOx ratio poses a potential risk of reducing the De-NOx performance. Therefore, De-NOx catalysts that are not affected by the NO_2/NOx ratio are needed. In response to this need, MHI developed a multifunctional De-NOx catalyst featuring both NH_3-NO_2 reaction and NH_3-NO reaction properties to reducing NOx with a high ratio of NO_2 content.

When the NO_2/NOx ratio is larger than 0.5, the steady De-NOx performance of the improved catalyst described above is equivalent to that of a conventional catalyst at high temperatures. At low temperatures, however, the De-NOx performance of a conventional catalyst drops substantially, while the performance of the improved catalyst is maintained at an acceptable level. As shown in **Figure 2**, the improved catalyst provides high, steady De-NOx performance, even if the NO_2/NOx ratio is 0.9. Furthermore, we have confirmed that the De-NOx performance of the improved catalyst is equivalent to that of a conventional catalyst under normal conditions where the NO_2/NOx ratio is low.

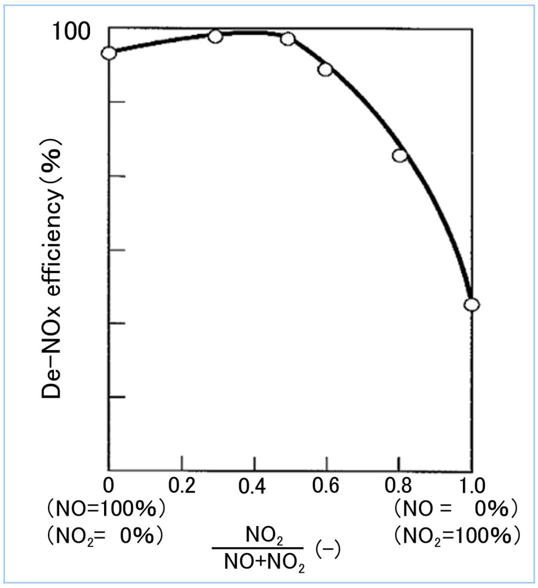

Figure 1 Correlation between NO_2/NOx ratio and De-NOx efficiency
De-NOx efficiency in response to changes in NO_2 ratio.

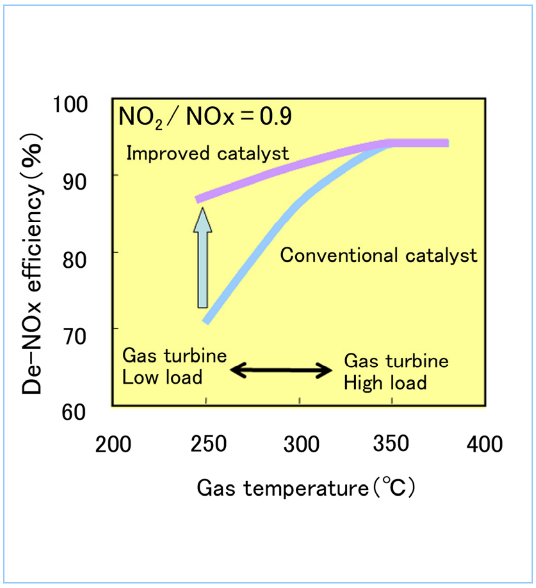

Figure 2 De-NOx performance of the improved catalyst intended for gas turbines, for NOx with a high ratio of NO_2 content
A conventional catalyst is compared with the improved catalyst.

The NO_2/NOx ratio in the exhaust gas from gas turbines increases during load drop, thereby posing the risk that NOx emissions will temporarily exceed the regulation value at the plant outlet. To eliminate this possibility, response control under high NH_3/NOx molar ratios is very important. The De-NOx speed of a conventional catalyst is slow when the NO_2/NOx ratio is high, and the NOx concentration at the catalyst outlet drops gradually in response to changes in the NH_3/NOx molar ratio, as shown in **Figure 3**. However, the De-NOx speed of the improved catalyst is extremely high when the NO_2/NOx ratio is high, and the NOx concentration at the catalyst outlet drops rapidly immediately after changes are detected in the NH_3/NOx molar ratio. The behavior is clearly different between a conventional catalyst and the improved catalyst.

In the final stage of development, the durability of the improved catalyst was evaluated by exhaust gas exposure tests in actual gas turbines in Japan and abroad. Securing of durability in actual exhaust gas environments is essential for commercialization of the catalyst. It was verified that MHI improved catalyst has good durability enough to commercialize after exposure tests of about 14,000 hours in total (**Figure 4**). The exposure tests proved that there is little decline in the De-NOx performance of the improved catalyst as is the case with a conventional catalyst intended for gas turbine power plants, and that the improved catalyst is remarkably stable and without any significant changes in properties.

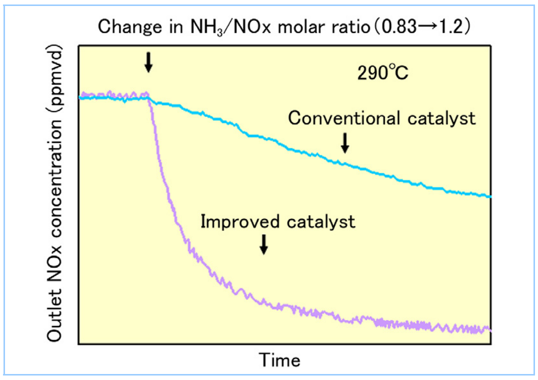

Figure 3 Results of tests for De-NOx reaction/response with changes in NH_3/NOx molar ratio
Responsiveness is compared between the conventional catalyst and the improved catalyst.

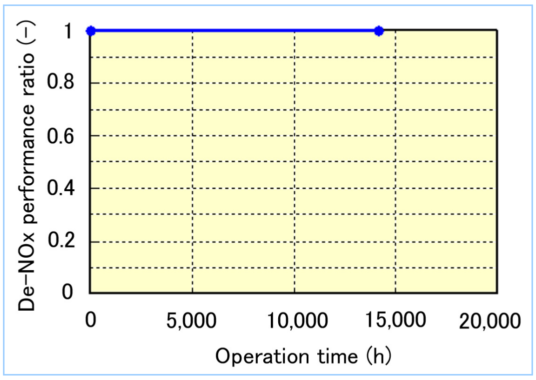

Figure 4 Results of actual gas exposure tests using the improved catalyst
The figure indicates that the De-NOx performance remains the same before and after exposure to actual gas.

3. Improvement and Development of Catalysts Intended for Coal-Fired Boiler Plant

If the fly ash generated by coal combustion passes through a honeycomb catalyst together with the exhaust gas, components in the fly ash, such as calcium, gradually adhere to the inner surface of the catalyst and block further De-NOx reaction on the catalyst surface. Furthermore, the fly ash will form partial sediments along the gas path in the catalyst and gradually prevent smooth passage of the exhaust gas. Eventually, complete blockage of the gas path occurs, causing deterioration of the De-NOx performance. Thus, De-NOx catalysts are periodically replaced in order to maintain De-NOx performance. However, fresh De-NOx catalysts are expensive because they contain rare metals such as titanium, tungsten, and molybdenum. This leads to the strong need for cost reductions in both the renewal of De-NOx catalysts and in the disposal of spent catalysts. Effective recycling of spent catalysts that were usually disposed would address this need. At the same time, catalyst recycling would lead to a reduction in the disposal of rare metals and contribute to global environmental conservation.

According to some information some spent De-NOx catalysts for coal-fired boiler plants are finely ground, formed into honeycombs, and calcined. That makes fly ash and its components, such as calcium, mixed in the honeycomb catalysts. Portions of the catalyst that have not deteriorated during the operation are distributed on the surface of catalyst to recycle spent catalysts.[3] Other recycling method was also proposed in which spent catalysts are crushed into fine powders, mixed with fresh materials, formed, and calcined, in an effort to reduce fly ash and components such as calcium mixed in the honeycomb catalysts.[4] In these methods, however, the regenerated De-NOx catalysts contain fly ash and other components, thereby reducing the catalyst component per gas contact area and showing lower the De-NOx performance than the fresh De-NOx catalyst. To improve performance, MHI developed regenerated catalysts that feature the De-NOx performance equivalent to that of fresh catalysts.[5] In the MHI method, the NOx performance was recovered by an activation treatment, in which fresh catalyst components were coated after removal of substances that caused deterioration. The renewed catalysts are classified into two types: type I, which employs spent catalysts removed from De-NOx reactors as the honeycomb substrates, and type II, which uses honeycombs made by forming ground product of spent catalysts as the substrates. In Type I, spent catalysts are employed as substrates without processing. Therefore, spent catalysts with severe cracks and damage cannot be recycled unless amount of the damaged catalyst are replaced with brand-new catalyst. In contrast, in type II, spent catalysts are crushed to produce raw materials, which are then formed into the honeycomb shape to create substrates. Therefore, damaged catalysts can be used effectively in type II structures. Catalysts manufactured by MHI do not contain inactive materials in the substrates, and the substrates consist almost totally of materials that exhibit catalytic activity. To maximize the advantage of recycling the entire honeycomb catalyst, spent catalysts are crushed into powders, which are then formed into the honeycomb shape with the cell width and length that meet the needs of customers. Through these methods, we succeeded in remarkably expanding the application range of replacement catalysts.

When spent catalysts are recycled, catalytic components are coated for activation, as described above. The coated layer on the honeycomb catalyst exhibits superior durability in the exhaust gas from coal-fired boilers, which contains a large amount of fly ash, because of the unique bimodal technology shown in **Figure 5**. Furthermore, the De-NOx performance of spent catalysts deteriorated is recovered nearly to the initial value by MHI's original regeneration technology, as shown in **Figure 6**, making it possible to recycle rare metals. With respect to the durability of the regenerated catalysts in long-term use, deterioration has been demonstrated to be not much faster than in conventional catalysts, and the products are in practical use today.

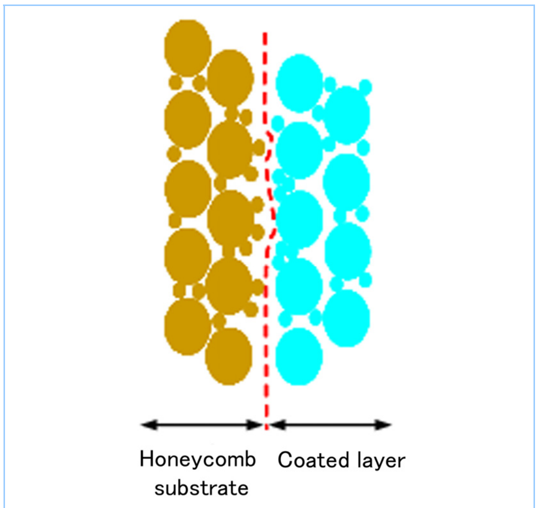

Figure 5 Pattern diagram of the regenerated catalyst
The honeycomb catalyst is covered with a coated layer. The sizes of the circles indicate the sizes of particles used for coating. The coated layer is stabilized by a unique bimodal technology.

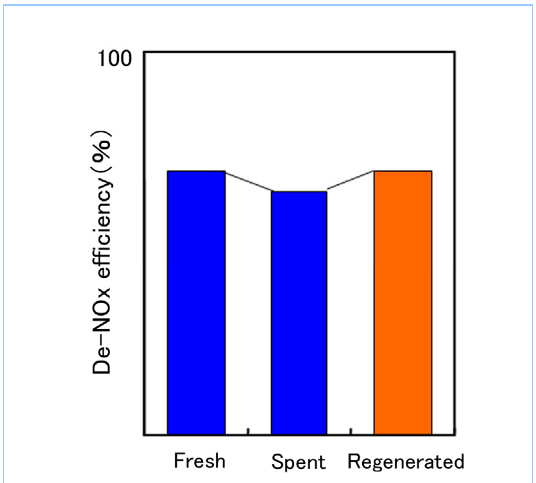

Figure 6 Comparison of De-NOx efficiency in a brand-new catalyst, a spent catalyst, and a regenerated catalyst
The figure indicates that De-NOx efficiency of the spent catalyst is inferior to that of the brand-new catalyst, while De-NOx efficiency of the regenerated catalyst is equivalent to that of the brand-new catalyst.

4. Conclusion

Emission control regulations have been tightened year after year throughout the world in consideration of environmental conservation. Under these circumstances, more sophisticated flue gas cleaning catalyst technologies are needed, and there is increased need for reduction of waste products and improved recycling of rare metals. To address these needs and to respond quickly to the wide range of customer needs in the global marketplace, MHI developed two unique types of catalysts for De-NOx: (1) a catalyst intended for gas turbine power plants with high NO_2/NOx ratios and (2) a regenerated catalyst intended for coal-fired power plants. Both types of catalyst have been commercialized. In the future, properties of exhaust gases treated by De-NOx systems will continue to change in response to diversification of fuels and improvements in the main units (boilers, gas turbines). MHI will continue to promote further developments, aiming to deliver De-NOx equipment with high reliability and economic potential.

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