

Kinetic Modeling Study of NO_x Conversion Based on Physicochemical Characteristics of Hydrothermally Aged SCR/DPF Catalyst

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ABSTRACT

Diesel engines have better fuel economy over comparable gasoline engines and are useful for the reduction of CO₂ emissions. However, to meet stringent emission standards, the technology for reducing NO_x and particulate matter (PM) in diesel engine exhaust needs to be improved. A conventional selective catalytic reduction (SCR) system consists of a diesel oxidation catalyst (DOC), diesel particulate filter (DPF), and urea-SCR catalyst. Recently, more stringent regulations have led to the development of SCR systems with a larger volume and increased the cost of such systems. In order to solve these problems, an SCR catalyst-coated DPF (SCR/DPF) is proposed. An SCR/DPF system has lower volume and cost compared to the conventional SCR system. The SCR/DPF catalyst has two functions: combustion of PM and reduction of NO_x emissions. As PM is removed from the DPF at high temperatures (>650°C), the SCR/DPF system is exposed to higher temperatures as compared with those in the conventional SCR system. In this study, we investigated the NO_x reduction performance and the properties of a hydrothermally aged SCR/DPF catalyst. Using these data, a model that can predict the NO_x conversion of the hydrothermally aged SCR/DPF catalyst was constructed. A commercial copper-exchanged zeolite catalyst, Cu-ZSM-5, was used and aged in synthetic air with 10% water over the temperature range 650-750 °C. The effects of hydrothermal aging on the catalysts were investigated using a synthetic gas bench, and a detailed analysis of the structure of the hydrothermally aged catalyst was performed. Using the experimental data, we succeeded in constructing a hydrothermally aged SCR/DPF model for predicting the NO_x conversion based on changes in the physicochemical characteristics of the catalysts with changes in the hydrothermal aging conditions. This work is the first step toward bridging the gap between a lab-simulated performance model and the global reactivity observed under real-world conditions.

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INTRODUCTION

Diesel engines have high thermal efficiency and constitute an important technology for the reduction of CO₂ emissions. On the other hand, particulate matter (PM) and nitrogen oxides (NO_x) are generated due to diesel combustion. In addition, exhaust gas regulations under real driving conditions will be enforced [1], so that further improvement of exhaust gas reduction technology is required. Diesel oxidation catalysts (DOC) [2], NO_x storage catalysts (NSC) [3, 4], urea selective catalytic reduction (SCR) systems [5, 6], and diesel particulate filters (DPF) [7] have been set to practical use as technologies for reducing exhaust (CO, THC, NO_x, PM). Recently, an SCR/DPF system combining SCR catalyst with DPF was developed to reduce the NO_x and PM emitted from diesel vehicles [8, 9, 10]. The SCR/DPF system is set at the rear of the engine; the distance between the engine and the SCR/DPF is shorter than that when a conventional SCR catalyst is used. Further, SCR/DPF is exposed to a high-temperature atmosphere due to regeneration of the DPF [11].

Previous study has focused on changes in the DPF performance due to deterioration of the SCR catalyst and the physical properties of the catalyst. There are numerous studies on qualitative correlations between the physical properties of an aged catalyst and deterioration of the catalyst performance [12, 13, 14]. However, there are only a few studies on quantitative correlation between the changes in physical properties and the changes in catalyst performance, when the catalysts are aged by various factors [15]. Recently, many models have been studied to predict the SCR catalytic performance. In addition, there are some studies on models to predict the performance of aged catalysts [16, 17, 18]. However, models to predict the performance of aged catalysts based on their physical properties have not yet been established. In order to construct a universal model to predict the performance of aged catalysts, it is important that the model is constructed based on the physicochemical properties of the aged catalysts. Therefore, it is necessary to clarify quantitatively the changes in the performance and physicochemical properties when the

SCR/DPF catalyst is deteriorated. This allows not only the prediction of the deteriorated catalyst performance but also the development of a high-performance post-treatment system.

The purpose of this study is to construct the model for the prediction of the deteriorated catalyst performance based on changes in the physical properties of the deteriorated catalyst. In this paper, we evaluated the effects of the different hydrothermal treatments on a commercial copper-exchanged zeolite catalyst. From the experiments, the rate constant of the SCR reactions and amount of ion-exchanged Cu were obtained. These values were used for the construction of the model to predict the performance of the deteriorated catalysts.

EXPERIMENTAL

Catalyst Samples and Hydrothermal Aging Method

The catalyst powder used in this study was Cu-ZSM-5 (zeolite structure, ZSM-5; SiO₂/Al₂O₃ ratio, 38; Cu loading, 3.6 wt% in terms of CuO). 100 g/L of catalyst powder was wash-coated on SiC-DPF (350 cell, 11 mil, φ 143 mm and length 127 mm) for investigation of the catalyst performance and measurement of the SCR reaction rate.

The test piece, which was cut from a full-size SCR/DPF, had a diameter of 25.4 mm and length of 127 mm. In order to investigate the performance of the hydrothermal aged catalyst, the catalyst powder and the test pieces were aged in an oven with flowing gas introduced at a flow rate of 1 L/min (10% H₂O, 10% O₂, and N₂ balance). The oven temperature was raised to 650, 700, and 750 °C at 10 °C/min and then maintained for a predetermined time, followed by cooling to room temperature. The aging times were set to 4 conditions, i.e., 5, 10, 20 and 30 h under each set of aging temperature conditions. In this paper, each sample is referred to as HT650 °C 5hr, 10hr, 20hr, 30hr (HT700 °C and HT750 °C). The fresh catalyst is denoted as Fresh.

Catalyst Analysis

X-ray diffraction (XRD) measurements were performed to analyze the change in catalyst structure caused by deterioration. Ultima IV (Rigaku Corporation) was used as the XRD apparatus with scans run between 2θ values of 3° and 90° at 20 degree/min. The conditions for X-ray output were 40 kV/30 mA. The XRD patterns were obtained three times under each set of experimental conditions and averaged for display.

In addition, in order to elucidate the change in the state of Cu due to hydrothermal degradation and the amount of Cu, H₂-temperature-programmed reduction (TPR) experiments were carried out. In the H₂-TPR method, the reduction profile of Cu was obtained by increasing the temperature at a gas composition of 5% H₂, Ar balance at 5 °C/min. From the results, the amount of ion-exchanged Cu was estimated using the equation (1).

$$Cu_{in} = \frac{A_{Cuin}}{A_{Cuall}} \times Cu_{all}$$

(1)

where Cu_{in} and Cu_{all} show the amount of ion-exchanged Cu and total Cu supported on the catalyst; A_{Cuin} and A_{Cuall} show the spectral area assignable to the ion-exchanged Cu and total Cu supported on the catalyst in the H₂-TPR, respectively.

EXPERIMENTAL PROTOCOL

The experimental apparatus for evaluating the performance of the hydrothermally aged catalysts is shown in Figure 1. This setup was used for measuring the conversion rate of the standard SCR, NH₃ oxidation, and NO oxidation. The flow rates of the various gases supplied from the cylinder were adjusted to a predetermined gas concentration shown in Table 1 using a mass flow controller at 40000 h⁻¹ SV, and the gases were introduced into the SCR/DPF test piece through a heating furnace. The concentrations of NO, NO₂, N₂O, and NH₃ were measured before and after the catalyst using FT-IR. Each reaction rate was measured at 500, 400, 300, 200, and 150 °C. The conversions were measured when the gas concentration was stabilized. The conversions of NOx, NH₃, and NO were calculated from the equation (2).

$$\eta_x = 100 \times \frac{x_{in} - x_{out}}{x_{in}} \quad (2)$$

where η_x shows the conversion, x_{in} shows the inlet gas concentration of catalyst, and x_{out} shows the outlet gas concentration of the catalyst. x denotes the gas species.

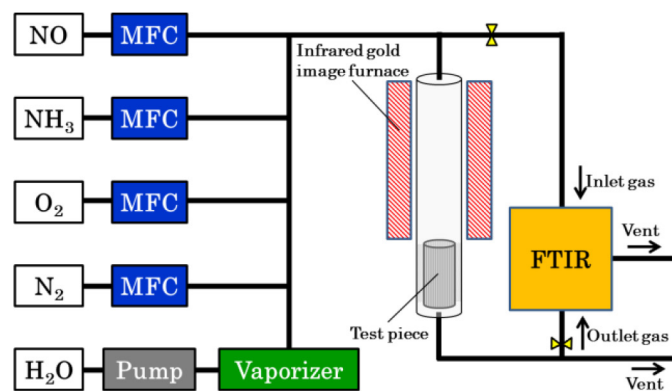


Figure 1. Schematic diagram of catalyst reactor system.

Table 1. Experimental Conditions.

	Standard SCR reaction	NH ₃ oxidation	NO oxidation
SV [h ⁻¹]	40000	40000	40000
NO [ppm]	300	0	300
NH ₃ [ppm]	300	300	0
O ₂ [%]	10	10	10
H ₂ O [%]	10	10	10
N ₂ [%]	balance	balance	balance

RESULTS AND DISCUSSION

Effect of Hydrothermal Aging on Standard SCR

Figure 2(a) shows the NO_x conversion over the catalysts hydrothermally aged at 650 °C for different degradation times at each reaction temperature (500, 400, 300, 200, and 150 °C) in the standard SCR process. The NO_x conversion decreases with increasing aging time below the reaction temperature of 300 °C. Above the reaction temperature of 300 °C, in the case of fresh, HT650 °C 5hr, and HT650 °C 10hr catalysts, the NO_x conversion decreased with increasing reaction temperature, while in the case of the HT650 °C 20hr and HT650 °C 30hr catalysts, the NO_x conversion increased with increasing reaction temperature. The NO_x conversion of the fresh catalyst was the worst among those for the experimental catalysts at the reaction temperature of 500 °C. Figure 2(b) shows the NH₃ conversion over the catalysts hydrothermally aged at 650 °C for different degradation times at each reaction temperature (500, 400, 300, 200, and 150 °C) in the standard SCR process. The NH₃ conversion decreased with increasing aging time, which was similar to the NO_x conversion below the reaction temperature of 300 °C. The NH₃ conversion increased with increasing reaction temperature, regardless of the aging time.

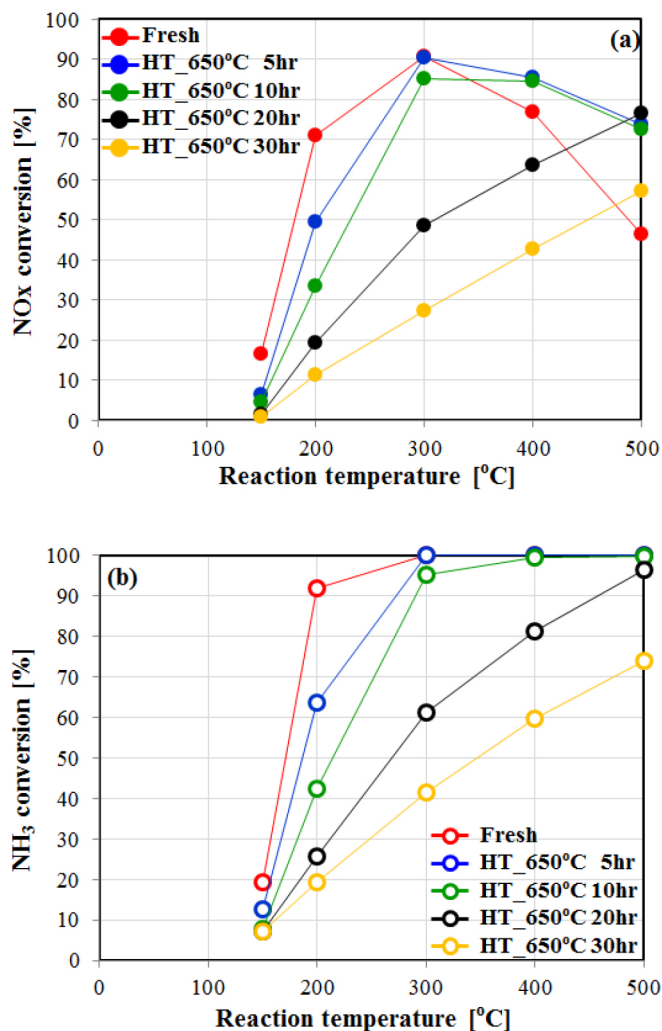


Figure 2. Aging time dependence of (a) NO_x and (b) NH₃ conversion of the catalyst aged at 650 °C in the standard SCR reaction.

Figure 3(a) shows the NO_x conversion over the catalysts hydrothermally aged at 750 °C for different degradation times at each reaction temperature (500, 400, 300, 200, and 150 °C) in the standard SCR process. Figure 3(b) shows the NH₃ conversion under the same conditions as those in figure 3(a). NO_x and NH₃ conversion showed the same tendency as that observed when the catalysts aged at 650 °C were used.

In the standard SCR experiments, a side reaction such as NH₃ oxidation occurred in addition to the main reaction for the reduction of NO_x. When NO is generated by the NH₃ oxidation reaction, it is difficult to determine the accurate NO_x conversion in the standard SCR reaction. Qualitative evaluation of the NH₃ oxidation reaction was performed over the aged catalyst at each reaction temperature (500, 400, 300, 200, and 150 °C) with NH₃ and O₂ as inlet feed gases.

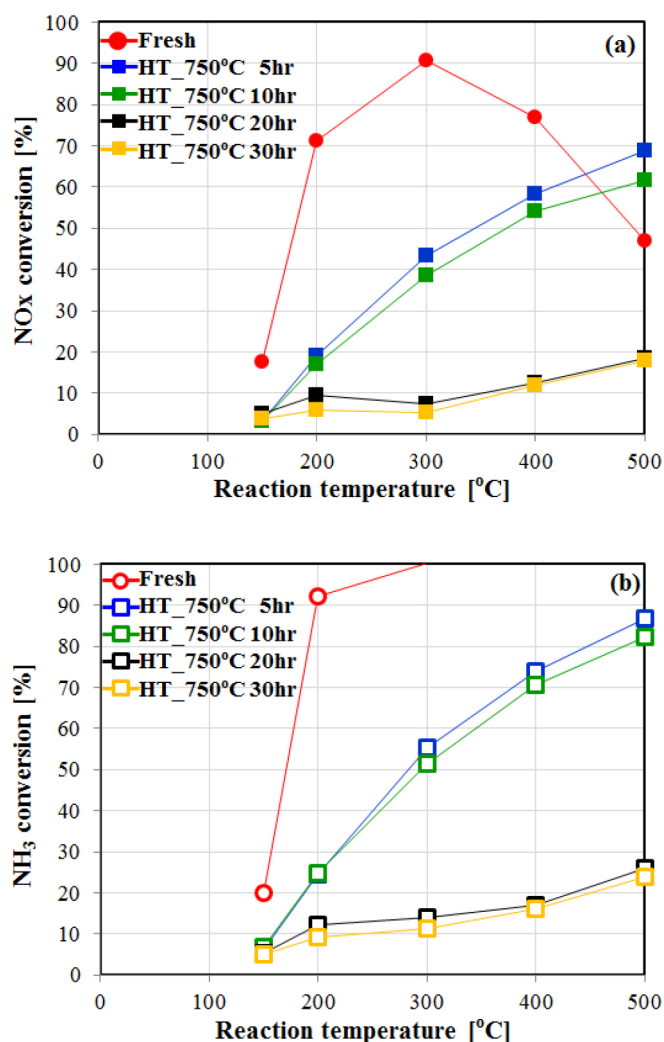


Figure 3. Aging time dependence of (a) NO_x and (b) NH₃ conversion of the catalyst aged at 750 °C in standard SCR reaction.

Effect of Hydrothermal Aging on NH₃ Oxidation

Figure 4(a) shows the rate of NH₃ oxidation when using the catalysts aged at 650 °C for different aging times. NH₃ oxidation activity was observed for all the catalysts above 300 °C. The NH₃ oxidation rate decreased as the degradation time increased. Figure 4(b) shows the NH₃ oxidation rate when using the catalyst aged at 750 °C. NH₃ oxidation activity was observed for all the catalysts above 300 °C. The NH₃ oxidation rate decreased as the degradation time increased.