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Characteristics of the simultaneous removal of PM and NO*x* using CuNb-ZSM-5 coated on diesel particulate filter

Wooseok Kang [a], Byungchul Choi [b,*], Hwanam Kim [b]

[a] School of Mechanical Engineering, Chonnam National University, 300 Yongbong-dong, Gwangju 500-757, Republic of Korea
[b] School of Mechanical Systems Engineering, Chonnam National University, 300 Yongbong-dong, Bug-gu, Gwangju 500-757, Republic of Korea

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ABSTRACT

The purpose of this study is to investigate the characteristics of the simultaneous removal of PM and NO*x* on the CuNb-ZSM-5 SCR/DPF catalysts coated onto DPF substrate. NO*x* conversion by the CuNb-ZSM-5 catalyst was higher than those by Cu- or Fe-ZSM-5 catalysts. NO*x* conversion of the SCR/DPF catalyst with a wall-flow (plugged) was considerably lower under 450 °C than that of the SCR/DPF catalyst with a channel-flow (unplugged). The de-NO*x* performance of the SCR/DPF catalyst coated with CuNb-ZSM-5 was highest among the catalysts examined. SCR/DPF catalyst coated with CuNb-ZSM-5 had superior PM oxidation performance compared to the other SCR/DPF catalysts.

1. Introduction

Improvement in the thermal efficiency of automotive engines will reduce the consumption of fossil fuels and contribute to the improvement of atmospheric environments on a global scale. Diesel cars are operated under lean-burn operation conditions, and have characteristics of excellent fuel efficiency and low CO_2 emission compared to gasoline cars. However, since diesel cars have higher concentration of particulate matter (PM) and nitrogen oxides (NO*x*) emission compared to gasoline cars, it is necessary to apply after-treatment systems to meet emission regulations like EURO-6.

Representative technologies for after-treatment systems to reduce NO*x* under lean-burn operation conditions such as diesel cars include lean NO*x* trap (LNT) and selective catalytic reduction (SCR) catalyst [1].

The urea-SCR system selectively purifies NO*x* over SCR catalyst by NH_3 produced by spraying urea into the exhaust pipe for pyrolysis and hydrolysis. Urea-SCR catalyst has advantages such as excellent NO*x* conversion, wide activation temperature range, and low system cost compared to LNT catalyst. The urea-SCR system is currently one of the most effective technologies for reducing NO*x* emission from diesel vehicles. However, the urea-SCR system for diesel vehicles has some problems, such as complexity due to the need for an additional urea dozing system, and high cost. Diesel vehicles also need an additional diesel particulate filter (DPF) device to remove PM. DPFs collects and regenerates PM through filtering with a 70–90% collecting ratio, and is known as the most effective among PM removal technologies [2,3]. DPFs are usually coated by a catalytic layer (Pt or Pd) that accelerates the PM and enables regeneration at lower temperatures. Such filters are called catalyzed diesel particulate filters (CDPFs) [4–6].

As CDPF and SCR catalysts have relatively large volume and heavy weight, their size should be reduced for installation or production cost reduction of parts. Some research on 2-way SCR/DPF with SCR catalyst coated on the DPF substrate has been partly undertaken [7–9]. 2-Way SCR/DPF (henceforth referred to as SCR/DPF) can improve the installation and reduce weight, volume, production processes and cost of catalysts by reducing the catalyst canning to one. The catalysts currently available applied to SCR/DPF are mostly based on Cu-ZSM-5. SCR/DPF using Cu-ZSM-5 has high PM regeneration temperature of 500–600 °C, so independent fuel spray is needed for active regeneration of PM in the DPF. There has been little in-depth research of the simultaneous removal of PM and NO*x* on SCR/DPF catalysts, especially research on PM oxidation at lower temperature. The purpose of this study is to investigate the characteristics of simultaneous removal of PM and NO*x* on CuNb-ZSM-5 SCR/DPF catalyst coated onto DPF substrate.

2. Experimental details

2.1. Preparation of catalysts

Cu-ZSM-5 and CuNb-ZSM-5 catalysts used for the test were prepared by conventional liquid-phase ion exchange method.

* Corresponding author. Tel.: +82 62 530 1681; fax: +82 62 530 1689.
E-mail addresses: srainbo2@lycos.co.kr (W. Kang), bcchoi@chonnam.ac.kr, bcchoi@jnu.ac.kr (B. Choi), aerocar@korea.com (H. Kim).

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Table 1
Properties of AC DPF substrate.

Melting temperature (°C)	Elastic modulus (GPa)	Porosity (%)	Mean pore size (μm)	Cell density (cell/in^2)	Wall thickness (mil)
2400	9.1	50	50	300	12

Commercial Fe-ZSM-5 catalyst (Sud-Chemie) was used. The ZSM-5 (Zeobuilder) used for the test was H-ZSM-5 with a Si/Al ratio of 17. The Si/Al ratio of Fe-ZSM-5 was 11. From preliminary study, it was determined that the optimal loading of copper (Cu) was 5 wt%. When the amount of Cu loading exceeded 5 wt% for the SCR catalyst, large CuO (copper oxide) particles were created on the catalyst surface, which had a bad effect on NO*x* conversion. 3 wt% of Nb was mixed with 5 wt% of Cu-ZSM-5 catalyst, which is presented as CuNb-ZSM-5. 3 wt% Nb loading was selected because de-NO*x* performance was best in this loading. Cu-ZSM-5 catalyst with 5 wt% of Cu was produced as follows. At room temperature, 1.26 g of $CuSO_4$ (Sigma–Aldrich) was put into 350 mL of distilled water at 80 °C and stirred for 30 min, and then a small amount of NH_4OH (25%) was added to adjust the pH to 8–8.5. Then, the solution was stirred for another 30 min. 10 g of ZSM-5 (Zeolyst, Si/Al atom ratio of 17) was put into the aqueous $CuSO_4$ solution. After a day of ion-exchange, the sample was filtered and washed with distilled water 3 times. After washing the solution twice, it was dried in an oven at 80 °C for 24 h. The production method of CuNb-ZSM-5 catalyst is equivalent to that of Cu-ZSM-5 catalyst except for adding 1.5 g of Nb precursor ($C_4H_4NNbO_9{\cdot}xH_2O$, Sigma–Aldrich). The catalyst powder was calcinated in air at a flow rate of 2 L/min for 2 h at 500 °C. Advanced Cordierite (AC) DPF substrates (Corning) were coated by dipping into respective fine powders of Cu-ZSM-5, CuNb-ZSM-5, and Fe-ZSM-5 (<1 μm in a diameter) of 80 g/L density. After dip-coating, the SCR/DPF catalysts were calcinated for 2 h again, while supplying air at 2 L/min and 500 °C. Table 1 shows the properties of the AC DPF substrate.

2.2. Experimental apparatus and method

The characteristics of NO*x* and PM removal of the SCR/DPF catalysts were evaluated using a laboratory-scale normal-pressure fixed-bed model gas catalytic reactor. Fig. 1 shows a schematic diagram of the experimental apparatus. The concentrations of the supplied model gases were controlled with a mass flow controller (MFC). The concentrations of the reaction and generated gases were measured by Fourier transform infrared spectroscopy (FTIR, I2004, Midac). The NO*x* conversion of the catalysts was obtained from Eq. (2.1)

$$\text{NO}x\ \text{conversion}\ (\%) = \left(1 - \frac{[\text{NO}x_{\text{out}}]}{[\text{NO}x_{\text{in}}]}\right) \times 100 \tag{2.1}$$

where $\text{NO}x_{\text{in}}$ is the inlet concentration of NO*x* and $\text{NO}x_{\text{out}}$ is the outlet concentration of NO*x* from the catalyst reaction part.

The temperature in front of the catalyst was measured by installing a K-sheath type thermocouple (Φ = 0.5 mm) located 5 mm in front of the catalyst center. Every catalyst was tested after flushing with nitrogen atmosphere at 500 °C with flow rate of 2 L/min for 60 min. Table 2 shows the composition of model gases to evaluate the catalysts. As assuming test conditions to be equivalent to a medium load in light-duty diesel vehicles, space velocity (SV) was set to 26,000 h^{-1}, and the concentrations of the supplied gases were set at O_2 10%, H_2O 1.5%, NO 500 ppm, and NH_3 500 ppm (standard SCR reaction condition). The performance of the SCR/DPF catalyst was evaluated under steady-state and transient state after supplying gas at 100 °C under the conditions shown in Table 2, and sufficiently saturating NH_3 for about 1 h. The experiment was carried out under a heating rate of 4 °C/min from 120 to 600 °C in transient conditions. The de-NO*x* performance of the SCR/DPF catalyst was evaluated under channel-flow (unplugged) and wall-flow (plugged) states. The channel-flow refers to a catalyst state with both the inlet and outlet of channel open like in general SCR or diesel oxidation catalyst (DOC) catalysts, while the wall-flow state refers to a catalyst substrate with characteristic checkerboard pattern created by open and plugged cells at the inlet and outlet. Adjacent channels in the wall-flow filters are alternatively plugged at each end, thus forcing the gas to flow through the porous walls, which act as a filter medium [10]. The pressure drop of the SCR/DPF catalyst was measured at three space velocity conditions of 13,000 h^{-1}, 26,000 h^{-1} and 36,000 h^{-1} as shown in Fig. 1.

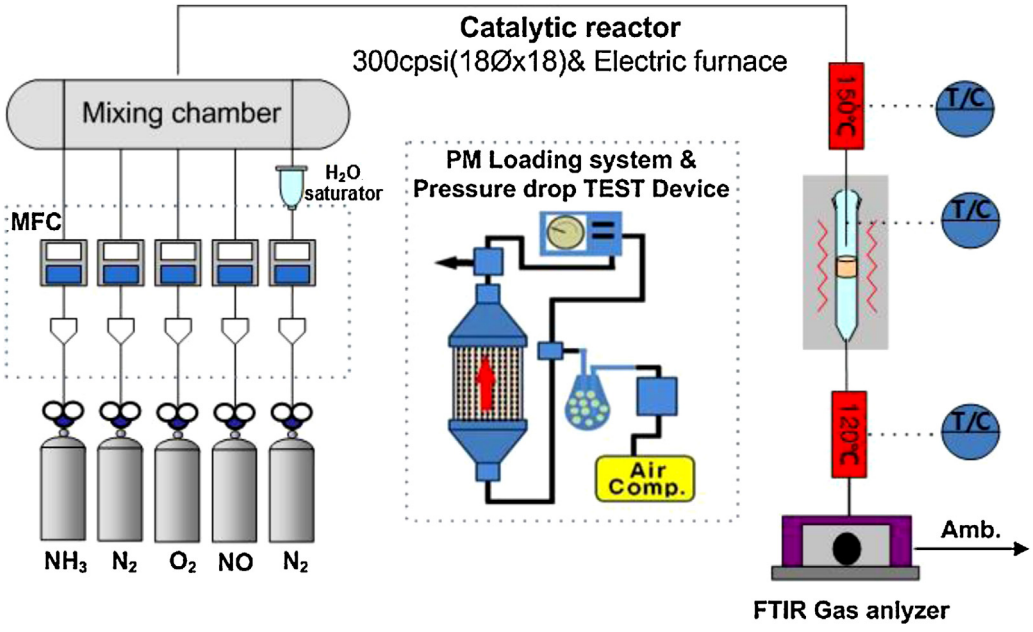

Fig. 1. Experimental apparatus for model gas catalytic reaction test.