

Volume Reduction of SCR Catalyst Using Zeolite-Base Honeycomb Substrate

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ABSTRACT

The method of converting NO_x with urea SCR is an effective solution for complying with the stringent NO_x emission legislations of the future, particularly in the case of heavy duty diesel vehicles. In order to broaden the freedom of SCR catalyst design and volume design, a honeycomb structure formed with metal ion exchanged zeolite(NCH: New Concept Honeycomb) and for comparison a wash-coat type structure (conventional catalyst) were prepared. The possible range of catalyst volume reduction in NCH was investigated by comparative measurement of NH₃ adsorption distribution, consumption behavior of adsorbed NH₃ within the structures, and of space velocity and NO₂/NO_x dependence of NO_x conversion efficiency. In addition, from NEDC evaluation in an engine bench, it was found that combining urea injection logic suitable for NCH results in equal or higher NO_x conversion efficiency and NH₃ slip characteristics with only 1/2 the volume of conventional catalyst structure. It was concluded that the application of NCH increases the degree of freedom in selecting the catalyst and designing the volume of catalyst.

INTRODUCTION

The application of selective catalytic reduction (SCR) system by injecting urea solution for reduction of NO_x emissions from diesel engines will contribute to fulfilling the stringent future NO_x emission legislation not only in the United States, European countries, and Japan, but also in China and India. The focus of developments is currently directed towards thermally durable catalysts[1,2], SO_x/HCs tolerant catalysts, and urea injection control strategies[3,4,5]. Hydrothermal durability of catalysts, in particular ion-exchanged zeolite, has been improved extensively by catalyst manufacturers. In general, hydrothermal deactivation in ion-exchanged zeolite catalysts is due to dealumination caused by aluminum bond

with H₂O[6]. The structure of acidic sites is modified so as not to be affected by H₂O[2].

In order to obtain high catalytic activity, not only is it important to improve the catalyst, but also the methods of using catalyst. For making the catalyst highly active; while storing large amount of NH₃ in a catalyst to the extent possible, urea injection control would be required so that NH₃ desorption does not occur due to rapid changes in temperature[7].

There are two main aspects regarding urea injection control logic. Injection of aqueous urea solution that actively accumulates as NH₃ in catalyst, and then injecting the aqueous urea solution equivalent to the amount of NH₃ consumed due to the inflow of NO_x in order to maintain the adsorption condition of NH₃. Our group have pointed out that high NO_x conversion efficiency at low temperatures would be realized by achieving the maximum high adsorption rate possible and maintaining the rate by injecting excessive aqueous urea solution to the extent that does not cause NH₃ slip[8]. In addition, it was found that by forming the honeycomb structure with Fe/β-zeolite, the amount of NH₃ that can be adsorbed is more than twice as compared to wash-coat type catalyst (hereinafter “conventional catalyst”)[9]. By utilizing these high NH₃ adsorption characteristics, the adsorption amount margin until NH₃ breakthrough can be increased with maintaining high NO_x conversion efficiency. Based on this, it is possible to expand urea injection control properties.

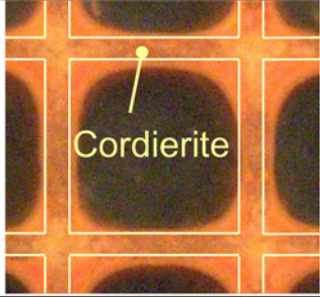
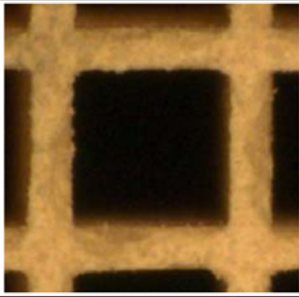
Another issue along with catalyst improvement and control logic is making the emission control system more compact. SCR system and DPF need to be integrated within the emission system in order to satisfy NO_x and PM emission regulations. Researches related to their



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Table 1. Cell dimensions comparison between conventional catalyst and NCH

	Conventional catalyst	NCH
Appearance		
Cell density	62 cells/cm ²	62 cells/cm ²
Wall thickness	0.10 mm (substrate) 0.20 mm (incl. coat)	0.28 mm
Cell width	1.17 mm (substrate) 1.07 mm (incl. coat)	0.99 mm
Aperture ratio	64.1 % (incl. coat)	60.8 %
zeolite amount	X	2X

combination(integration type or separation type) are being actively pursued[10,11,12,13,14]. When applying the urea SCR system into various types of vehicles in future, it would be important to expand the freedom of SCR catalyst design and reduce its volume.

In this study, NH₃ adsorbed-NCH and -conventional catalyst were divided into four parts and then NH₃ adsorption distribution was evaluated by measuring the amount of desorbed NH₃ in each part. Moreover, how the adsorbed NH₃ was used in each structure was evaluated by feeding a certain amount of NO_x into each catalyst in which NH₃ was adsorbed. As a result, it was found that NH₃ was adsorbed through the front part of the catalyst and the anterior division of the honeycomb mainly contributes to NO_x reduction. In addition, the results of the synthetic gas bench and engine bench test indicated that by combining an optimum injection logic with NCH that exhibits twice as much absolute NH₃ adsorption as the conventional catalyst, it is possible to reduce the volume of NCH by 50% compared to the volume of conventional catalyst. Based on this conversion efficiency test and pressure loss assessment, it was concluded that the design window of catalyst and catalytic support volume can be expanded.

SYNTHETIC GAS BENCH TEST

SAMPLE PREPARATION

A honeycomb structured catalyst having Fe/ β -zeolite as a main constituent material combined with a binding agent and a reinforcing material was prepared. As a comparative sample, a conventional structure in which a catalyst layer of the above-mentioned Fe/ β -zeolite was formed on a cordierite

support by wash-coating was prepared. Its aperture ratio was measured by the image analysis and the Fe/ β -zeolite amount per unit honeycomb volume was half of NCH. Cell dimensions of prepared samples are summarized in [Table 1](#). After processing each sample to $\phi 25.4$ mm(1 inch) and L76 mm(3 inch), hydrothermal durability treatment was conducted for 60 h at 700 °C under the atmosphere of O₂: 10 vol.% and H₂O: 10 vol.%.

<[table 1](#) here>

NH₃ ADSORPTION MECHANISM

Test factors and levels for verifying the NH₃ adsorption distribution inside the honeycomb are shown in [Table 2](#). NH₃ was adsorbed in each sample under the following conditions: temperature = 150 °C; SV = 35,000 h⁻¹; NH₃: 350 ppm; N₂: balance. The amount of adsorbed NH₃ approximately corresponded to 20, 50 and 100% of the saturated NH₃ amount in each sample. Following this, the sample was equally divided into four parts and assigned numbers to each part from 1 to 4. The temperature of each part was increased consecutively from 25 to 450 °C at the rate of 10 °C per minute in N₂ atmosphere. The amount of NH₃ adsorbed in each part was evaluated by measuring the amount of NH₃ desorbed during heating.

Table 2. Factors and levels for NH₃ adsorption mechanism evaluation

Factors	Levels
Substrate	NCH structure, Conventional structure
Part	#1, #2, #3, #4
NH ₃ adsorption ratio	20%, 50%, 100%

Figures 1(a) and 1(b) shows the amount of NH₃ adsorbed in each part of NCH and the conventional catalyst. Here the adsorption ratio is defined as ratio of the amount of adsorbed NH₃ divided by the saturated NH₃ adsorption amount. When the amount of NH₃ adsorbed in NCH and the conventional catalyst for each part is compared, NCH shows about two times the NH₃ adsorption characteristics for every adsorption ratio. This is because the zeolite contained in each unit volume of NCH is almost two times as much as the conventional catalyst. At the same time, if the adsorption ratio of each part for the saturated NH₃ adsorption amount is compared at adsorption ratio of 20%, it is approximately 40%, 30%, 10%, and 1% from part 1 to 4 for both NCH and the conventional catalyst. Moreover, at adsorption rate of 50%, the adsorption ratio of each part is 70%, 60%, 40% and 15% from part 1 to part 4. Based on these results, it becomes clear that the same kind of concentration gradient is formed from front to rear of the honeycomb irrespective of structural differences. There have been reports that this kind of behavior was demonstrated from mathematical modeling as well[15].

CONSUMPTION MECHANISM ADSORBED NH₃

The mechanism how the adsorbed NH₃ is used in each part was studied when NO_x is passed through a catalyst having the NH₃ concentration gradient. Condition of adsorbed NH₃ consumption test is shown in Table 3.

Table 3. Adsorbed NH₃ consumption test condition

Item	Condition
Sample size	φ1 inch x 3 inch L
Aging	fresh
Temp.	150°C(SCR inlet)
SV	35,000hr ⁻¹
Evaluation gas	NO: 350ppm, CO ₂ : 5 vol.%, O ₂ : 14 vol.%, H ₂ O: 10 vol.%, N ₂ : balance

50% of the saturated adsorption amount of NH₃ was adsorbed to NCH and the conventional catalyst at 150 °C in N₂ atmosphere. After that, synthetic gas, the composition of which is shown in Table 3, was introduced to the honeycomb

for 3 min and 1.5 min in NCH and the conventional catalyst, respectively. In order to find out the distribution of remaining NH₃ that did not react with NO_x; similar to the method described in the preceding section, the sample was divided into 4 parts and the amount of desorbed NH₃ was measured in each part.

The amount of NH₃ adsorbed in each part of NCH and the conventional catalyst before and after NO_x introduction are shown in Figures 2(a) and 2(b). Consumption of the adsorbed NH₃ by SCR reaction is highest at the inlet part that had adsorbed the largest amount of NH₃. From this, it is found that the consumption of adsorbed NH₃ reduces according to NH₃ adsorption concentration distribution. In addition, it is also found that NH₃ consumption ratios in each part of the NCH and the conventional catalyst were the same irrespective of the differences in catalyst structure. Based on these results, when NH₃ is adsorbed until breakthrough, most of the NH₃ is adsorbed in the front part of the honeycomb and NO_x conversion expressed by the following reaction rate equation also occurs mainly in the front part.

$$v = k[NO_x]^A[NH_3]^B \quad \text{Eq. (1)}$$

As compared to a conventional catalyst, since NCH adsorbs larger amounts of NH₃ to the front part of the honeycomb, when a specified amount of NO_x is passed through SCR catalyst, larger amount of NO_x can be reduced in the front part of the honeycomb. Therefore, NCH with the same catalyst and the same volume as a conventional catalyst would always exhibit higher performance. This also indicates that NCH with the same catalyst and smaller volumes as compared to a conventional catalyst exhibits equivalent or higher NO_x conversion efficiency.

VALIDATION OF SCR CATALYST VOLUME REDUCTION

In this section, we discuss the possibility of SCR catalyst volume reduction range by the application of NCH as well as the range of volume reduction. In the present experiment, 3 inch-long NCH and the conventional catalyst, and 1.5 inch-long NCH were prepared. All these samples had undergone 60 h hydrothermal treatment at 700 °C. After raising the temperature of the catalyst to 175 °C under N₂ atmosphere, synthetic gas containing NO_x: 350 ppm (NO₂/NO_x = 0, 0.5), NH₃: 525 ppm, O₂: 14 vol.%, CO₂: 5 vol.%, H₂O: 10vol.%, N₂: balance was introduced into the catalyst and the outlet gas concentration was measured. The volume flow rate of the synthetic gas was 22.5 l/min.

Figures 3 and 4 show the calculated NH_3 adsorption amount dependence of NO_x conversion efficiency at $\text{NO}_2/\text{NO}_x = 0$ and 0.5. The calculated NH_3 adsorption amount was obtained by subtracting the amount of NH_3 consumed during SCR reaction with NO_x and the discharged NH_3 amount from the introduced NH_3 amount. Initial behavior of NO_x conversion efficiency is similar for NCH and the conventional catalyst irrespective of differences in catalyst size and NO_2/NO_x . At the same time, when NH_3 adsorption amount is 0.1g, NCH has higher NO_x conversion efficiency than the conventional catalyst despite the fact that 1.5 inch long NCH has almost the same amount of catalyst as the conventional catalyst. Moreover, 3 inch long and 1.5 inch long NCH show almost equivalent both NO_x conversion efficiency at $\text{NO}_2/\text{NO}_x = 0.5$ that causes “Fast SCR”. As mentioned in the previous section, NH_3 is mainly adsorbed to the front part of the honeycomb and NO_x is mainly reduced at the front part of the honeycomb. Since high $\alpha(=\text{NH}_3/\text{NO}_x)$ condition is created locally in NCH, even 1.5 inch long NCH shows higher efficiency than the conventional catalyst.

NO_x conversion efficiency depends on temperature, SV and NO_2/NO_x . The required NCH volume for which it shows equal catalyst performance as the conventional catalyst was studied under a certain temperature, SV and NO_2/NO_x condition. In the present experiment, Fe/ β -zeolite catalyst supplied by a different manufacture was used. Prepared samples were also subjected to the same hydrothermal treatment as mentioned above. Table 4 shows factors and levels in this evaluation.

Table 4. Factors and levels of catalyst volume reduction test

Factors	Levels
Catalyst structure	NCH, Conventional
NH_3/NO_x	1.0, 1.5
NO_2/NO_x	0, 0.25, 0.5
SV(hr^{-1})	35,000, 70,000, 140,000

After completely desorbing the NH_3 from the catalyst for each measurement, the evaluation gas (NO_x : 350 ppm, NH_3 : 350 or 525 ppm, O_2 : 14 vol.%, CO_2 : 5 vol.%, H_2O : 10 vol.%, N_2 : balance) was introduced and NO_x conversion efficiency was measured when outlet NH_3 concentration was 10 ppm. Figures 5 and 6 show some of the results for $\text{NO}_2/\text{NO}_x = 0.25$, and $\alpha = 1.0, 1.5$. Since the reaction rate increases with increasing temperature and the reaction takes place in the proximity of the wall surface, geometric specific surface area of the honeycomb gradually becomes the dominant factor for conversion efficiency. The superiority of NCH decreases as the zeolite present inside the wall is not utilized; however, for the same volume, NCH still shows higher conversion

efficiency than the conventional catalyst (catalyst volume can be reduced in case of the same conversion efficiency).

Figure 7 shows the map of the catalyst volume of NCH required for allowing it to have equal conversion efficiency as the conventional catalyst at $\alpha = 1.0, 1.5$ (the conventional catalyst volume is taken as 100%). As the temperature increases and NO_2/NO_x approaches 0.5, the required volume ratio increases. This is because the increase of reaction rate brings the rate-limiting step closer to the mass transfer rate-limiting region. In this case, it is beneficial to increase the amount of NH_3 supply[16]. In case of $\alpha = 1.0$, although around 80% volume is required when the temperature is over 300 °C and the NO_2/NO_x ratio is in the proximity of 0.5, at $\alpha = 1.5$ the required volume ratio can be brought down to 30-40%. Since the catalyst inside the wall of NCH can also contribute to the reaction, injecting large amounts of urea solution(increasing the supply rate of NH_3) within the range where NH_3 slip does not occur is even more beneficial than the conventional catalyst. By combining the injection logic that effectively uses the front part of catalyst, it might be possible to reduce the catalyst volume.

NEDC EVALUATION

In this section, the possibility of volume reduction in NCH as compared to a conventional catalyst is evaluated under the actual exhaust gas condition.

SAMPLE PREPARATION

Fe/ β -zeolite-based NCH segments with approximate cross-sectional area of 35 mm $\times$ 35 mm were assembled by using ceramic cement. The outer surface and length of the sample were cut in 5.66 inch diameter and 4 inch length. Aperture ratio of the sample containing adhesive layer was approximately 55%. As a comparative sample, a commercial sample consisting of a Fe/ β -zeolite-based SCR catalyst wash coated onto a cordierite substrate(hereinafter market catalyst) was prepared. The outer surface was cut in 5.66 inch diameter. By combining two pieces of 2 inch and 6 inch, 8 inch long sample was prepared. Based on image analysis, aperture ratio of the market catalyst was found to be around 56%. NCH had almost an equal amount of Fe/ β -zeolite but volume was half compared to the market catalyst.

EVALUATION SET-UP AND TEST PROCEDURE

Figure 8 shows a schematic image of the evaluation system set-up used for engine bench test. After stuffing a catalyst into a can, it was thermally treated by 2 h at 700 °C in air. A DOC(1.46 litter) and a DPF(3.3 litter) were arranged upstream of a SCR catalyst, and an aqueous solution of urea was injected into exhaust gas after DPF. Swirler and Mixer were arranged upstream and downstream, respectively, of the