

Verification of HC Trap Materials and Catalysts to Reduce Exhaust Emissions during Cold-start in V6 Engine

Hiroki TAKEORI¹

Koji NEMOTO²

Yuki OKU¹

Ryohei IKUTOMO¹

Keita NAKAO³

Toyohiro USUP³

ABSTRACT

In order to reduce emissions immediately after engine cold-start, which is a challenge for conventional three-way catalyst systems, an HC trap catalyst was developed that combines new HC trap materials and an HC purification catalyst for efficiently purifying the trapped HC. Ag-CHA and Cu-FAU were developed as zeolite HC trap materials that have pore sizes close to the HC molecular sizes and can adsorb HC up to higher temperatures by increasing the stability of the exchanged ions that promote chemisorption. It was also clarified that arranging the HC purification catalyst layer in the upper layer of the HC trap materials is key to effectively purifying the desorbed HC, and that adding an oxygen absorbing and releasing material consisting of CeO₂ and ZrO₂ in a 1:1 ratio to the HC purification catalyst enables purification of the desorbed HC even under stoichiometric conditions. A V6 engine with this HC trap catalyst in an underfloor arrangement was able to reduce HC emissions during engine cold-start by approximately 50% in the LA#4 mode emission test.

1. Introduction

Automotive exhaust gas regulations, which began in the United States in the 1960s, have been gradually tightened to the present, and this trend is expected to continue going forward. This has been addressed in gasoline engines by the invention and evolution of the three-way catalyst (TWC). However, as TWC does not manifest purification functions until reaching the light-off temperature (the temperature at which the purification rate reaches 90%), the exhaust gas is emitted without purification from immediately after engine cold-start until the TWC light-off temperature is reached. As it generally takes several tens of seconds for TWC to reach the light-off temperature, technology for purifying these emissions during cold-start is key for coping with ever tighter emission regulations.

Although lowering the TWC light-off temperature has been studied for many years⁽¹⁾⁻⁽⁴⁾, it is not easy and there is a limit to what TWC can do looking ahead to further tightening of regulations, so innovative technologies with different approaches will be needed. Numerous examples of

such research have been reported, including an electrically heated catalyst (EHC) that promotes early light-off by using electric power to heat the catalyst before engine cold-start⁽⁵⁾, and HC trap catalysts that adsorb (trap) the hydrocarbon (HC) components in exhaust gas in materials with pore sizes close to the HC molecular sizes such as zeolite at the low temperatures during engine cold-start, and then desorb and purify the HC after reaching the catalyst light-off temperature⁽⁶⁾⁻⁽¹¹⁾. This HC trap catalyst (HCTC) consists of trap materials and an HC purification catalyst as shown in Fig. 1, and has a simple structure with the trap layers additionally coated on a TWC. This has the advantage of not requiring changes to the existing exhaust layout or installation of additional systems.

While there have been numerous reports on trap materials, the performance is insufficient, and further enhancement is needed in anticipation of tighter regulations going forward. The authors therefore developed an HCTC that can reduce HC emissions from an inline 4-cylinder 1.5 L turbocharged direct-injection (DI) engine by approximately 50% in the LA#4 mode. This was achieved

¹ Innovative Research Excellence

E-mail: hiroki_takeori@jp.honda

² Honda Motor Co., Ltd.

³ Tosoh Corporation

by optimization of zeolites for the exchanged ions to maintain adsorption of the various sizes of HC contained in exhaust gas up to high temperatures⁽¹²⁾. However, large-displacement V6 engines have a higher exhaust flow rate than L4 engines, which increases the treatment amount per unit of time. This lowers the purification rate, and the slower rise in the exhaust gas temperature also lengthens the time until the light-off temperature is reached. As a result, emissions during cold-start increase and can account for 90% of total emissions⁽¹³⁾⁻⁽¹⁵⁾. Thus, while HCTC are expected to provide a high reduction effect immediately after cold-start, performance demands on HCTC are also increasing, such as an increased adsorption amount and a higher adsorption rate per unit time due to the greater flow rate, making it necessary to demonstrate the reduction effect of HC traps under such harsh environments. Therefore, this study verified the influence and effect of the HCTC arrangement in the exhaust layout of a V6 engine.

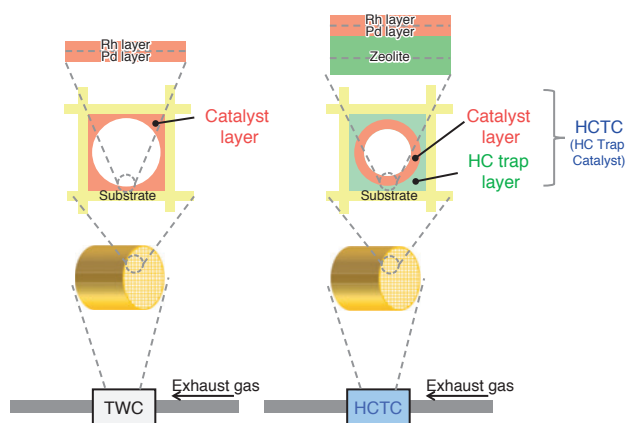


Fig. 1 HC trap catalyst configuration

2. HC Trap Goals

Consider the goals for increasing the emission reduction effect. First is to increase the adsorption amount in order to reduce the large emissions amount immediately after cold-start. Second is to purify the adsorbed HC without desorbing it as much as possible so as not to lessen the reduction effect. Third is to maintain the TWC purification performance other than immediately after cold-start at the same level as the TWC alone. Figure 2 shows the target purification characteristics of an HCTC that achieves these goals, and the following four points can be given as challenges.

- (1) The HC contained in exhaust gas include three types with different chemical bonds and structures: paraffins, olefins, and aromatics. In addition, each type has carbon numbers ranging from 1 to 9, in other words a distribution of sizes, which calls for the efficient adsorption of these diverse HC.

- (2) If the trapped HC are not retained until the purification start temperature of the co-used HC purification catalyst is reached, they may desorb and be emitted without purification, necessitating the ability to retain adsorbed HC until the purification start temperature or higher.
- (3) The adsorbed HC are purified by the HC purification catalyst, but the trap performance or purification performance is greatly influenced by how the HC trap materials and the HC purification catalyst coexist. This makes it necessary to maximize the adsorption and purification performance by optimizing the balance between the arrangement and amounts of both.
- (4) At the stoichiometric air-fuel ratio (A/F: stoichiometry), only the amount of oxygen needed for the three-way reaction is supplied, so there is zero oxygen after the TWC. This means that when the trapped HC desorbs, the condition with insufficient oxygen for purification results (A/F: rich), so some method is needed to supplement oxygen in order to maintain desorbed HC purification performance.

To address these issues, this study approached challenge (1) with the concept that the use of zeolites with pore sizes close to the HC molecular sizes is expected to increase the trapping probability at low temperatures and enhance the adsorption rate, making it important to select appropriate zeolite materials. An effective approach for challenge (2) was thought to be to enhance the adsorption force between the HC and the zeolite. Specifically, it was thought that desorption could be effectively suppressed by chemisorption, whereby ion species are introduced to the zeolite to enhance the electrostatic interactions with HC that have high electron densities such as those with double and triple C-C bonds (= aromatics and olefins). Effective approaches for challenges (3) and (4) were thought to be optimization of the HC trap material and HC purification catalyst layer arrangement and the catalyst coating amount to enhance HC purification performance, and the use of oxygen storage capacity (OSC) material with oxygen absorption and release functionality.

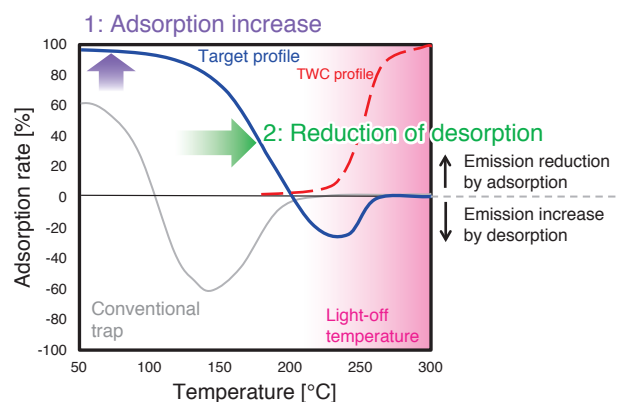


Fig. 2 Direction of enhancement of HC trap material

3. Trap Materials

3.1. Analysis of HC Composition

First, in any approach to the trap materials, it is important to understand what kinds of HC are contained in the exhaust gas, so the exhaust gas during engine cold-start was sampled and gas chromatography was used to analyze the HC composition. The detailed method is as follows. A sampling pipe was branched at a position 30 mm from the rear end of the TWC of an inline 4-cylinder 1.5 L turbocharged DI engine, a Tedlar bag was connected a sampling box under depressurization by a pump, and exhaust gas was sampled in each interval of 0-20 seconds, 20-50 seconds, and 50-150 seconds. HC qualitative and quantitative analysis was performed by gas chromatography.

Figure 3(a) shows the transition in the composition of the HC in the exhaust gas after passing through a TWC relative to the time from cold-start, classified into the three types of paraffins, olefins, and aromatics. HC here refers to non-methane organic gases (NMOG), which is the current regulatory criterion in the U.S. state of California. Each value is the relative value of the concentration in each interval with the total NMOG concentration (ppmC) from 0-20 seconds set to 100%. This shows that the emissions for the 0-20 seconds interval are three times the total for the 20-150 seconds interval, which is to say the first 20 seconds accounts for over 70% of the total. Furthermore, Fig. 3(b) shows the emission ratios of each carbon number and HC species relative to the total concentration (ppmC) in the 0-20 seconds interval. Characteristics of a wide size distribution with carbon numbers ranging from 2 to 9,

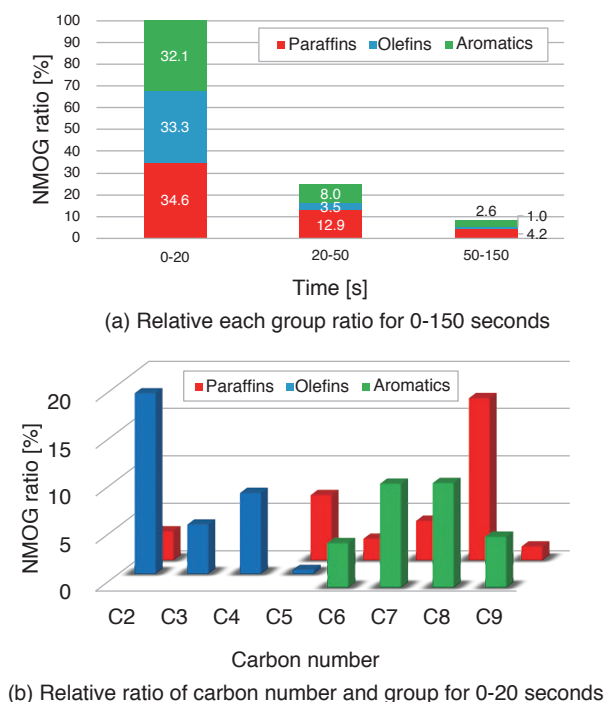


Fig. 3 HC Composition in rear part of TWC

and high ratios of C2-C4 small molecule olefins, C7-C8 aromatics, and C8 paraffins were confirmed.

Based on these results, the direction for enhancing the adsorption amount can be classified in terms of molecular size into C2-C4 small molecule HC and C7-C8 large molecule HC. It was decided to efficiently enhance physical adsorption by selecting two zeolites with pore sizes that match the respective molecular sizes. Next, regarding the direction for suppressing HC desorption, there is a high ratio of HC species with double bonds, namely aromatics and olefins, so chemisorption using the aforementioned exchanged ions is considered effective^{(6), (10)}. However, exchanged ions have a general tendency to thermally degrade, so it is important to consider heat resistance in the selection.

3.2. Selection of Trap Materials (Zeolite)

Zeolites that effectively trap the analyzed HC were investigated. H-type FAU, BEA, MFI, and CHA zeolites made by Tosoh Corporation, as well as these materials ion-exchanged with Ag, Cu, Cr, Co, Ni, and Mo, were used as HC trap materials. Figure 4 shows the structure and pore size of each zeolite used⁽¹⁶⁾. Various zeolites are classified by their framework structure, and each is named with three uppercase letters. Adsorption performance and purification performance were evaluated using a model gas prepared by mixing the gases from various cylinders, etc. at the specified ratio. The model gas for evaluation was mixed by controlling the flow rates of the various cylinders and vaporized liquid HC (toluene, isooctane) to achieve the composition shown in Table 1, and then flowed into the samples as simulated exhaust gas. The gas flow rate was set to 25 L/min (equivalent to SV 50,000 h⁻¹), and the temperature rise rate was set to 40°C/min. The purification rate was calculated using Eq. (1), and the inflow HC concentration was set to 1200 ppmC.

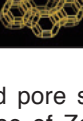
Zeolite	Structure	Pore size [nm]
CHA		0.37
MFI		0.47
BEA		0.60
FAU		0.74

Fig. 4 Structure and pore size of each zeolite (cited from Database of Zeolite Structures)

Table 1 Gas composition of model gas for evaluation

Gas	Concentration
Propylene / ppmC	348
Isopentane / ppmC	108
Toluene / ppmC	408
Isooctane / ppmC	336
NO / ppm	500
H ₂ / %	0.17
CO / %	0.5
O ₂ / %	0.49
CO ₂ / %	14
H ₂ O / %	10
N ₂	Balance

Adsorption rate [%] =

$$\left(1 - \frac{\text{Catalyst exhaust HC concentration}}{\text{Catalyst inflow HC concentration}}\right) \times 100 \quad (1)$$

Figure 5 shows the adsorption rate of H-type zeolites with various pore sizes for paraffins of each carbon number. In order to confirm the relationship between the zeolite pore size and the adsorption rate by HC molecular size, zeolites with pore sizes close to the molecular sizes of small and large HC in the exhaust gas are used, and the pore size in order from the smallest is CHA < MFI < BEA < FAU. The samples used for measurement were prepared by making a slurry of each zeolite powder and coating it onto $\Phi 25.4$ mm $\times$ 60 mm (30 cc) cordierite honeycombs which were then calcinated for 2 hours at 500°C. Instead of the model gas composition in Table 1, this evaluation used the simple composition of only a paraffin (one type with a carbon number from 3 to 8) at 300 ppmC and nitrogen and was conducted sequentially for carbon numbers from 3 to 8. The results confirmed that HC with a molecular size close to the pore size tend to be more easily adsorbed. Based on this,

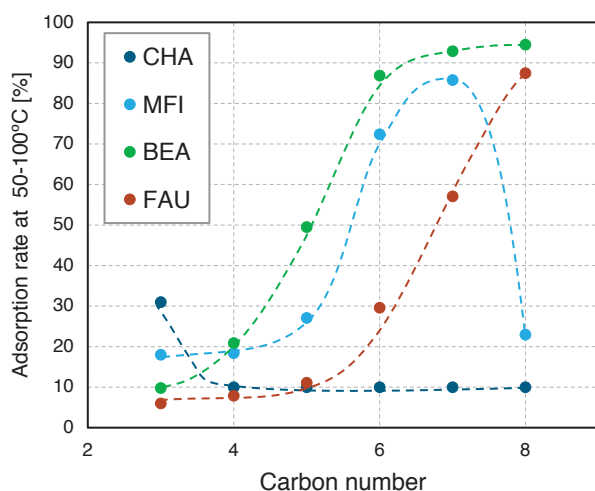


Fig. 5 Influence paraffin carbon number on adsorption rate of various zeolites evaluated with 300 ppmC various paraffin and N₂ gases

Table 2 Propylene adsorption rate on various ion-exchanged FAU

Element	Cu	Ag	Cr	Co	Ni	Mo
Adsorption rate [%]	5.1	13.0	-	-	-	-

CHA and MFI were selected as candidate zeolites for small-molecule HC, and BEA and FAU for large-molecule HC.

Next, exchanged ions for promoting chemisorption were individually selected for small- and large-molecule HC.

3.3. Selection of Exchanged Ion for Adsorption of Small-Molecule HC

First, in order to select the exchanged ion for small-molecule HC, various exchanged ions were introduced to FAU zeolite and the measured HC adsorption amounts were compared using propylene, which is a small-molecule HC. There have been reports on adsorption with small HC molecules using transition metal ions^{(17), (18)}, but there are few studies on HC trap materials that include heat resistance, so this was actually confirmed. Table 2 shows the results, with only Cu and Ag confirmed to exhibit adsorption performance, with Ag in particular providing the highest adsorption performance, so Ag was selected as the exchanged ion for small-molecule HC.

The performance of Ag zeolite was then evaluated. The heat resistance of exchanged ions is known to vary depending on the combined zeolite type⁽⁷⁾, and it is important to evaluate performance after aging. The conditions were set to a temperature (850°C) equivalent to underfloor arrangement, with an atmosphere alternating between flows of propylene-oxygen mixed gas for 80 seconds and air simulating fuel cut for 20 seconds, while simultaneously adding water to maintain a constant 10 vol%. Figure 6 shows the results of evaluating the propylene adsorption performance before aging (Fresh) and after aging of Ag-CHA and Ag-MFI, which are actual candidate zeolites for small molecules with Ag introduced. As shown in Fig. 6(a), fresh Ag-MFI exhibited higher adsorption performance than fresh

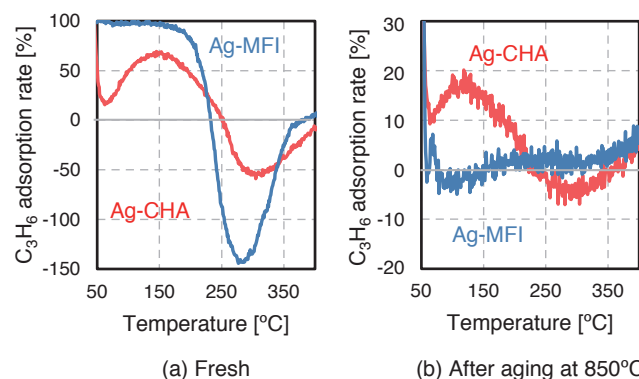


Fig. 6 Propylene adsorption and desorption profile of Ag-CHA and Ag-MFI

Ag-CHA, whereas after aging, the Ag-MFI adsorption function disappeared but Ag-CHA maintained its adsorption function as seen in Fig. 6(b). To analyze these factors, changes in the Ag ion and the zeolite states were analyzed. Figure 7 shows the Ag ion and cluster ratios obtained by ultraviolet-visible absorption spectroscopy (UV-Vis) as a physical property after aging. Figure 7(a) shows that CHA has smaller variation in the ratios before and after aging, whereas Fig. 7(b) shows that Ag aggregation progressed on MFI. Previous reports confirmed that X-ray diffraction (XRD) also showed that CHA exhibited smaller variation in crystallinity fluctuation before and after aging⁽¹⁹⁾. This suggests that Ag on CHA is more stable, which in turn helps stabilize the zeolite structure, enabling retention of adsorption functions.

3.4. Selection of Exchanged Ion for Adsorption of Large-Molecule HC

Next, focusing on materials for C5 or higher large-molecule HC, particularly aromatics, exchanged ions similar to those in Section 3.3. were introduced to FAU zeolite and the HC adsorption amounts were compared. Figure 8 shows the adsorption rate measurement results,

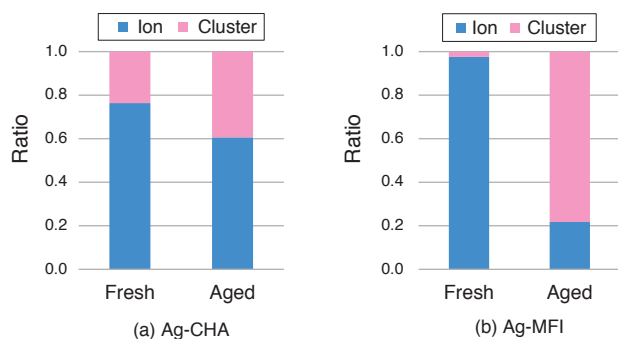


Fig. 7 Variation of Ag ion and cluster ratio calculated from UV-Vis spectra before and after aging

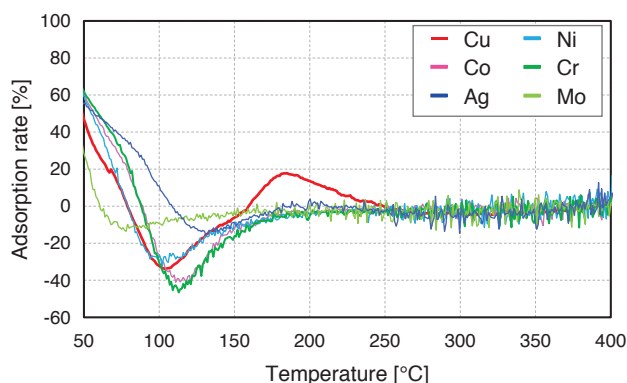


Fig. 8 Profile of HC adsorption on various ion-exchanged FAU after aging

which reveal that Cu alone has unique adsorption characteristics in the temperature range from 150 to 300°C. Reports thus far of adsorption as HC trap materials only concerned adsorption observed with ions other than Cu in the temperature range from 50 to 150°C, and this specificity of Cu is noteworthy. This adsorption characteristic on the high-temperature side is thought to be effective for delaying HC desorption, so Cu was selected as the exchanged ion for large molecules. This adsorption is observed only in the presence of water and disappears in its absence; that is, there is known to be an action of Cu and water⁽²⁰⁾. Also, like Ag, Cu is compatible with zeolite regarding to heat resistance, so the HC adsorption performance before and after aging was compared for materials where Cu was ion-exchanged with the candidate zeolites for large molecules. Figure 9 shows the results, and while both materials exhibit a second adsorption peak in the fresh state, only Cu-FAU retains it after aging. Therefore, to clarify the differences in the changes in the ionic state in each zeolite, the focus was placed on Cu degradation after aging, and the total amount of Cu^+ and Cu^{2+} ions in Cu-FAU and their ratio to CuOx were analyzed by electron spin resonance (ESR). Identification of each ion was performed by making use of the property that the measurable ions differ in the presence and absence of water, and it was assumed that all the Cu ions in the fresh state and the entire ion reduction amount after aging are CuOx. As shown in Fig. 10(a), it was confirmed that after aging, 1/3 of the Cu was oxidized and 2/3 retained the ionic state. Furthermore, the relationship between the Cu ion ratio and the second adsorption rate was investigated using FAU with various silica-alumina ratios ($\text{SiO}_2/\text{Al}_2\text{O}_3$ of zeolite) and Cu content, and the adsorption rate tended to decrease as the Cu ions decreased (and CuOx increased) as shown in Fig. 10(b). This is also thought to indicate that the ability to maintain adsorption performance after aging is related to the Cu ion retention state.

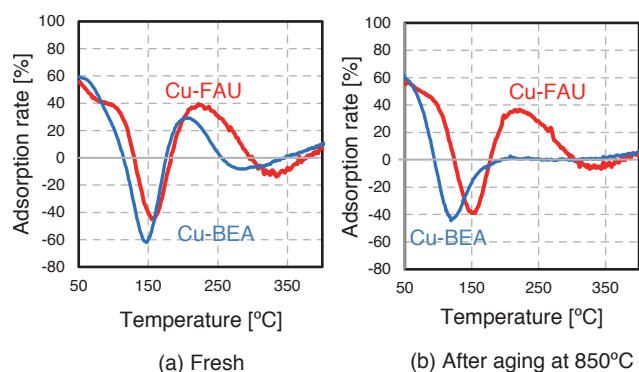


Fig. 9 THC adsorption and desorption profile of Cu-FAU and Cu-BEA

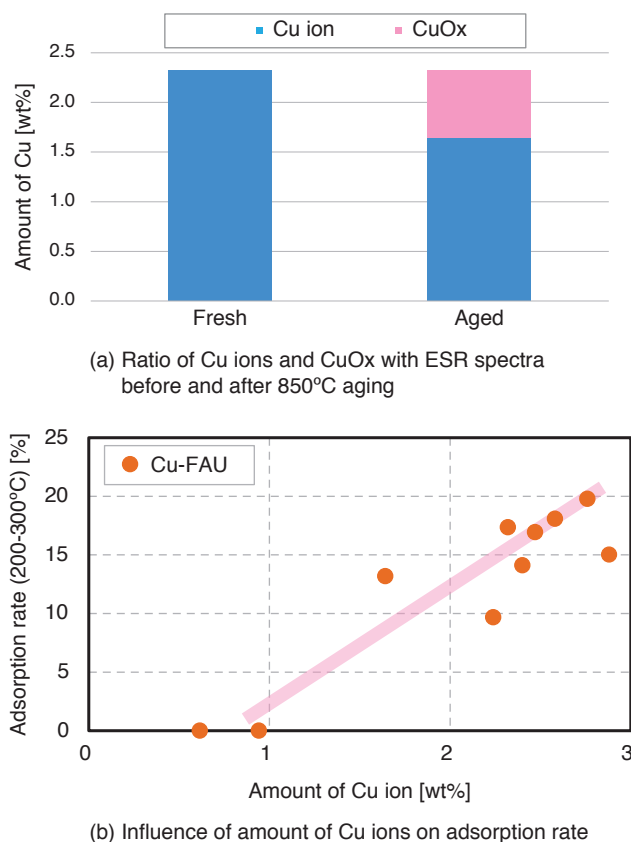


Fig. 10 Change in Cu ion after aging

3.5. Factors Enhancing the Heat Resistance of Exchanged Ions

It was found that the aforementioned Ag-CHA and Cu-FAU can maintain adsorption functions even after aging, and the main factor for this is thought to be that the zeolite enhanced the stability of the exchanged ion. There are multiple reports on the specific stability of Cu^{2+} ions under hydrothermal aging in CHA^{(21), (22)}, and it has been concluded from simulation analysis that this is due to the more stable interaction between the D6R unit and Cu^{2+} ions in the zeolite framework. In addition, Ag has an electron arrangement similar to that of Cu (one electron in the outermost s orbital and all 10 electrons in the inner d orbitals filled), so the interaction with the D6R unit is also estimated to be similar. Figure 11 shows model drawings of

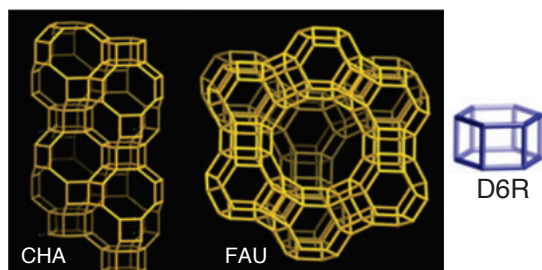


Fig. 11 D6R units in CHA and FAU

the CHA and FAU frameworks⁽¹⁶⁾, and it can be considered that CHA and FAU both exhibited heat resistance because they both have this D6R that stabilized the exchanged ion.

4. HC Trap Catalyst

The Ag-CHA and Cu-FAU selected as the HC trap materials were combined with an HC purification catalyst to make an HCTC that completes the process from adsorption to purification. This attempt aimed to achieve an HCTC that makes the most of the adsorption and purification functions.

The catalyst production method was as follows. $\gamma\text{-Al}_2\text{O}_3$ made by Sasol Ltd. was used as the Pd support material, and ZrO_2 and $\text{CeO}_2\text{-ZrO}_2$ made by DAIICHI KIGENSO KAGAKU KOGYO CO., LTD. were respectively used as the Rh support material and OSC material. Pd and Rh were supported on the support materials by an impregnation method using salt solutions of each, dried for 12 hours at 200°C, and then calcinated for 2 hours at 500°C to obtain Pd/ Al_2O_3 and Rh/ ZrO_2 powders. These powders were then made into slurries and coated in the specified amounts onto cordierite honeycomb similarly to the HC trap layer.

The methods of addressing the HC purification catalyst challenges described in Chapter 2 (3) and (4) were examined in detail. First, regarding the balance between adsorption and purification, the adsorption and purification performance vary widely depending on the HC trap layer and HC purification catalyst arrangement and amounts. For example, coating the HC purification catalyst on the upper layer side of the trap may result in either lower or higher trap performance. In addition, the coating amount increases by the amount of the trap layer compared to the currently used TWC, so the gas path narrows, leading to a higher gas flow rate (linear velocity) per unit of cross-sectional area of the gas path. This is expected to increase the treatment amount, which in turn may lead to lower adsorption and purification performance. The key is how much these declines in performance can be suppressed and how efficiently the trap effect can be linked to enhancement of the reduction rate.

Next is purification during HC desorption. Here, a lower HC purification rate due to insufficient oxygen leads to an increase in emissions. Use of an OSC material with oxygen absorption and release functionality in the TWC to compensate for this oxygen deficiency was examined.

4.1. Balance between Adsorption and Purification

4.1.1. Layer arrangement of HC trap materials

First, a layer arrangement that can make advantageous use of the HC trap material properties was considered. Based on the material properties, Cu-FAU exhibits interaction with water, so it should be arranged in the upper layer where there is higher probability of contact with water, whereas Ag-CHA adsorption is hindered by water, so arrangement in the lower layer is considered advantageous. Also, considering the ease of diffusion of

large HC molecules within zeolites, if Ag-CHA, which has a pore size smaller than the molecule size, is arranged in the upper layer, large HC molecules will be unable to enter the zeolite pores, thereby lowering the probability of contact with the Cu-FAU arranged in the lower layer. Therefore, a layout with Ag-CHA in the lower layer is expected to be preferable. Figure 12 shows the HC adsorption characteristics as an HC trap layer that combines the materials. Here, (a) shows the case with Cu-FAU arranged in the upper layer and Ag-CHA in the lower layer, and (b) shows the case with the opposite arrangement. As expected, case (a) was confirmed to have a better adsorption rate.

4.1.2. HC trap layer and HC purification catalyst layer arrangement

Next, the effect of the relative arrangement of the HC trap materials and the HC purification catalyst on adsorption and purification was compared. Figure 13 shows the adsorption and purification profiles when equal amounts of HC trap and HC purification catalyst are arranged vertically on the honeycomb. The profiles for the TWC alone and the HC trap layer alone are also shown for comparison.

Here, the HC purification catalyst layer is 150 g/L. When the HC trap layer is in the upper layer, a slight advantage in adsorption can be confirmed, but the purification performance is noticeably lower than the TWC. On the other hand, when the HC purification catalyst is in the upper layer, there is a slight drop in both adsorption and purification, but the impact on purification is less than when the HC trap materials are in the upper layer. This drop in purification performance when the HC purification catalyst is in the lower layer is thought to be largely due to lower gas diffusivity and the delayed temperature rise because of an inability to receive heat directly from the gas. Therefore, in consideration of the total reduction rate, it is important to position the HC purification catalyst in the upper layer.

4.1.3. HC purification catalyst coating amount

The HC trap layer described in section 4.1.1. was set to 200 g/L, which provides the greatest adsorption effect and

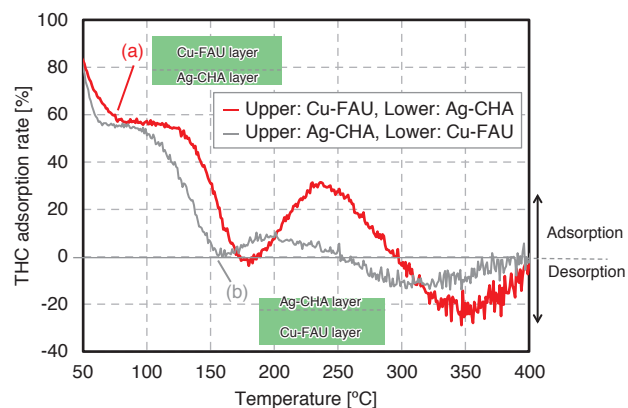


Fig. 12 Relationship between layer composition and adsorption of Cu-FAU and Ag-CHA and TWC

is equivalent to the coating amount of the currently used TWC. Therefore, if the HC purification catalyst coating amount is equal to that of the TWC, the total will be twice the current amount. Together with the height of the zeolite, the gas flow path will become quite narrow, leading to an increase in the aforementioned linear velocity and adversely affecting adsorption and purification. Therefore, guidelines for the HC purification catalyst are needed.

Figure 14 shows the relationship between the HC purification catalyst layer coating amount and the adsorption rate, purification rate, and reduction rate with the HC trap layer coating amount constant at 200 g/L. Here, the adsorption rate, purification rate, and reduction rate

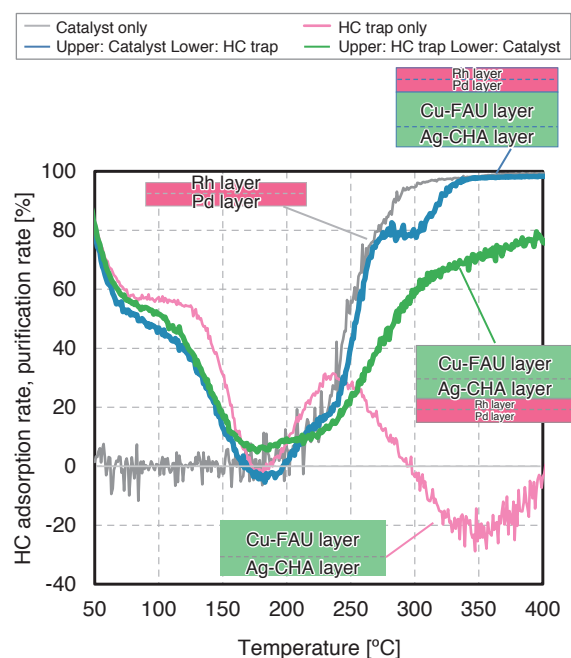


Fig. 13 Effect of zeolite-TWC arrangement on adsorption rate and purification rate

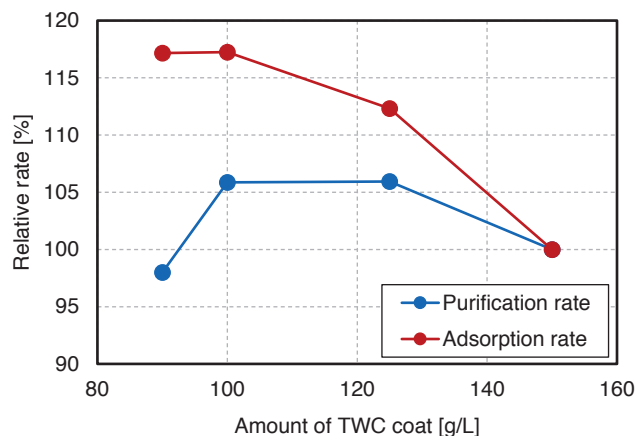


Fig. 14 Relationship between TWC coat and HC absorption rate, purification rate, and reduction rate

are expressed as relative values with the values at 150 g/L set to 100. In addition, the total amount of PGM for each sample was constant at 185 g/ft³. This figure shows that the adsorption rate exhibits a monotonically increasing trend as the coating amount decreases, indicating that the coating amount of the HC purification catalyst layer in the upper layer has a large influence. Meanwhile, the purification rate shows an initially rising trend as the coating amount decreases, but then turns downward at 100 g/L or less, indicating a tendency to have a maximal value. Figure 15 shows the linear velocity (calculated from the cross-sectional area of the gas path) and the Pd particle size (by the CO adsorption method) relative to the coating amount. Here, the linear velocity is observed to decrease together with the coating amount, indicating that the reaction proceeds more readily. In contrast, the particle size of the Pd, which serves as the active site of the reaction, was confirmed to aggregate with the increase in the Pd density as the coating amount decreases, resulting in lower catalytic activation. This suggests that this characteristic has a maximal value due to the trade-off relationship between these two factors. The above results indicate that it is effective to arrange the HC purification catalyst in the upper layer and the HC trap materials in the lower layer, and to set the HC purification catalyst coating amount to an optimal value to achieve the maximum purification rate value.

4.2. Material Selection Based on OSC

Purification of the desorbed HC is described using the results in Fig. 16. The vertical axis represents the TWC light-off temperature in the model gas performance evaluation test, and the horizontal axis represents the concentration of oxygen in the model gas. Normally, at the stoichiometric A/F, just the precise amount of oxygen needed for the purification reaction of the TWC is supplied, providing conditions for achieving the greatest purification performance. The reference temperature in this figure is set to 285°C, which is the light-off temperature of the reference TWC under stoichiometric conditions. In contrast,

the light-off temperature of the HCTC was confirmed to be 322°C, which is more than 30°C higher. The factor for this is that in the HCTC, although HC that desorbs in the light-off temperature range needs to be oxidized together with the HC contained in the exhaust gas, it is thought that the reaction does not readily proceed due to insufficient oxygen supply in actual operation. It was therefore thought that by adding oxygen in the model gas by the amount needed to purify the desorbed HC, the light-off temperature would return to the original level. An equivalent oxygen concentration was added and tested in the same manner, and the light-off temperature was confirmed to return to the same level as the reference TWC. This clearly indicates that the issue is insufficient oxygen, which placed the focus on how to supplement the oxygen needed for the desorbed HC.

Attention was thus turned to the OSC material, which is one of the main components used in TWC. In order to maintain the state in the TWC near A/F stoichiometry that provides the highest purification rate even in A/F fluctuations, the oxygen excess or deficiency at that time is compensated by the oxygen absorption and release function of the OSC material, thereby suppressing purification rate fluctuations⁽²³⁾. This function was also considered to be an effective means in this study, and helped to enhance the desorbed HC purification performance in terms of increasing oxygen supply with the OSC material. The approach was the CeO₂ ratio in the OSC material. The OSC material mainly comprises a composite oxide of CeO₂ and ZrO₂, which has two aspects: an oxygen adsorption and release function by the valence change of CeO₂, and a function to enhance heat resistance by crystal stabilization of ZrO₂. Therefore, the CeO₂/ZrO₂ ratio was examined that enables retention of heat resistance while helping to increase the oxygen supply during HC desorption. The OSC retention time was used as an indicator of the oxygen supply amount. The OSC retention time was evaluated by maintaining a flow of 0.5% oxygen (nitrogen balance) for 5 minutes in the 600°C steady state to fill the OSC material with oxygen, and then switching to 1% CO (nitrogen balance) to establish and maintain the zero-oxygen state

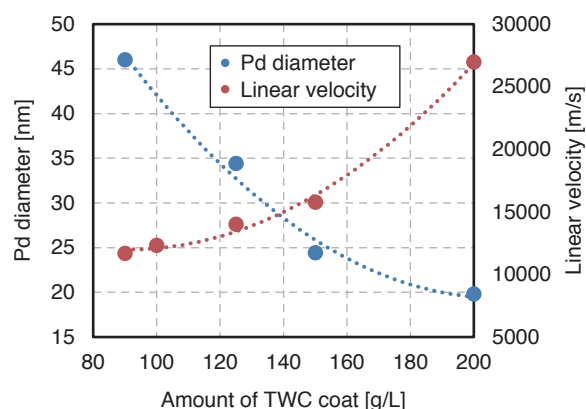


Fig. 15 Influence of coating amount on Pd particle size and linear velocity

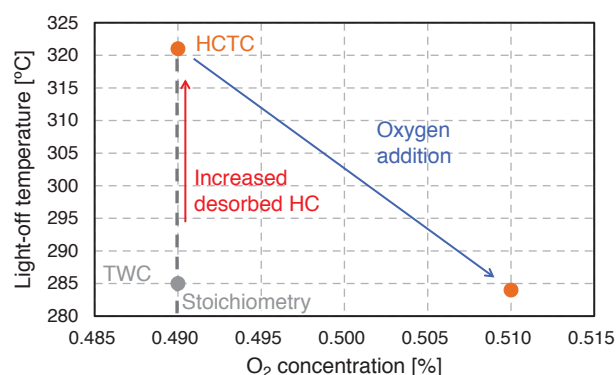


Fig. 16 Effect of oxygen concentration on desorbed HC purification temperature

for 5 minutes. That is, the OSC retention time indicates how many seconds the oxygen in the OSC material can continue to be supplied to oxidize CO and is defined here as the duration until the CO purification rate drops to 50%. The blue plots in Fig. 17 show the results of confirming the relationship between the CeO_2 ratio and the OSC retention time and reveal that the OSC retention time was longest at a CeO_2 ratio of 50%. The reason is thought to be that when the CeO_2 ratio is above this level, the ZrO_2 ratio drops, promoting thermal degradation of the CeO_2 . Conversely, when below this level, the lower CeO_2 ratio means that less oxygen can be supplied. Furthermore, a similar tendency was confirmed in the relationship between the CeO_2 ratio and the HC purification rate (Fig. 17, 2nd vertical axis, brown plots, purification rate in the interval from 200 to 400°C). In other words, it was indicated that increasing the amount of oxygen supply extends the OSC retention time and is effective for purification of desorbed HC.

Figure 18 compares the performance before and after

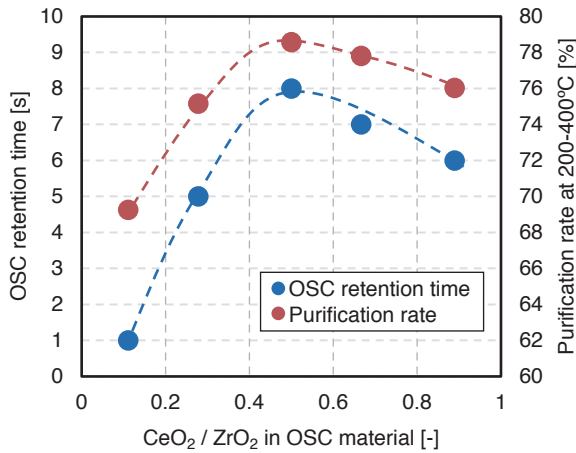


Fig. 17 Relationship between CeO_2 ratio, OSC retention time, and HC reduction rate

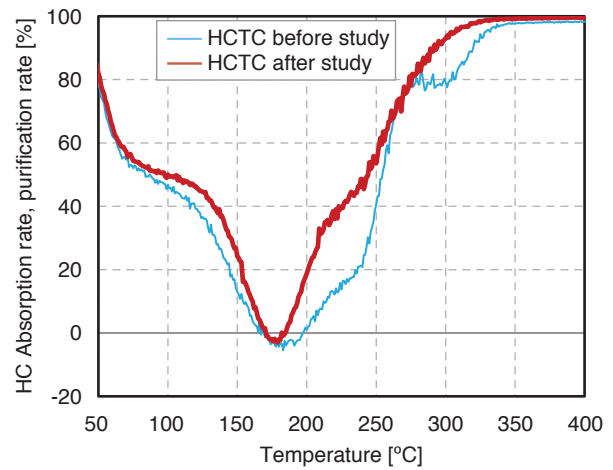


Fig. 18 Effect of HCTC study on temperature characteristics

optimizing the HC purification catalyst coating amount and the $\text{CeO}_2/\text{ZrO}_2$ ratio of the OSC material based on the above results. It was confirmed that the decline in adsorption and purification performance can be suppressed by setting the HC purification catalyst coating amount within the range that has both the smallest impact on adsorption and the lowest catalyst degradation, and by setting the CeO_2 ratio in the OSC material to maximize the desorbed HC purification rate.

5. Emission Reduction Effects in a V6 Engine

Figure 19 shows the HC trap system of a V6 engine based on the results of the above HC trap material and HCTC examinations. One TWC is placed close-coupled to the exhaust outlets of the three cylinders on each side, so there are no changes in the close-coupled layout, and the TWC installed underfloor in a conventional V6 engine is

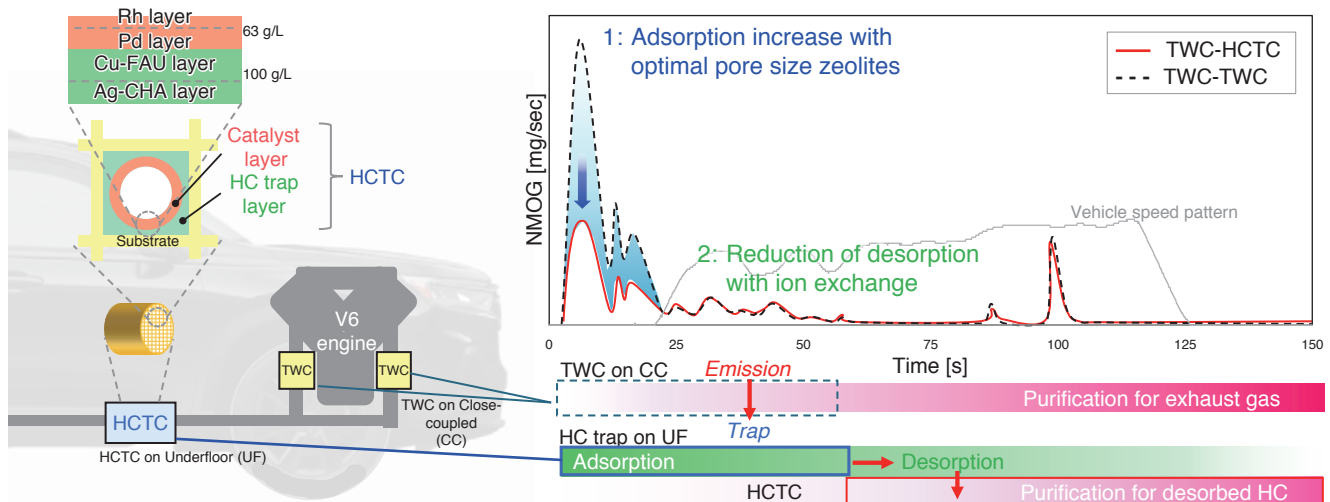


Fig. 19 Emissions reduction strategy using HCTC

replaced with the HCTC. The following purification scheme was devised based on this arrangement. In the 0-20 second interval, the exhaust gas passes through the unlit close-coupled TWCs but is adsorbed by the underfloor HCTC. In the 20-50 second interval, the close-coupled TWCs light-off, but the HC trap layer in the HCTC continues to retain the initially adsorbed HC. Then, in the 50-150 second interval, the gas flowing in from the engine is purified by the mostly activated TWC. Meanwhile, the adsorbed HC begins to desorb from the HC trap layer, but the HC purification catalyst layer of the HCTC is also activated, enabling purification of the desorbed HC.

5.1. Emission Test

The arrangement characteristics and the reduction effects in the final form were verified with an actual engine. The engine was a V6 3.5 L DI engine with LEV III certification gasoline used as the fuel. An identical TWC (PGM 140 g/ft³, aging equivalent to close-coupled (with only the temperature changed to 950°C in the previously described aging conditions), honeycomb cell density 600 cell/inch², cell wall thickness 3.5 mil, and capacity 0.85 L was installed close-coupled to each bank. A TWC (PGM 185 g/ft³, aging equivalent to underfloor arrangement, honeycomb cell density 400 cell/inch², cell wall thickness 3.5 mil, and capacity 1.0 L) was arranged underfloor as a reference, and evaluation was performed by replacement with the HCTC. The exhaust gas test was conducted in the LA#4 (cold-start) mode, and the HC used NMOG.

5.2. Characteristics of HC Trap Material and HC Purification Catalyst Arrangement

First, the effects of the optimal arrangement and volumes of the HC purification catalyst and the HC trap materials, which are the HCTC components, were compared in an actual engine. Figure 20 shows the comparison results (the HC purification catalyst is noted as CAT). Here, the vertical axis represents the reduction rate based on the emission values from 0 to 300 seconds with a TWC as the underfloor unit. Note that all arrangements

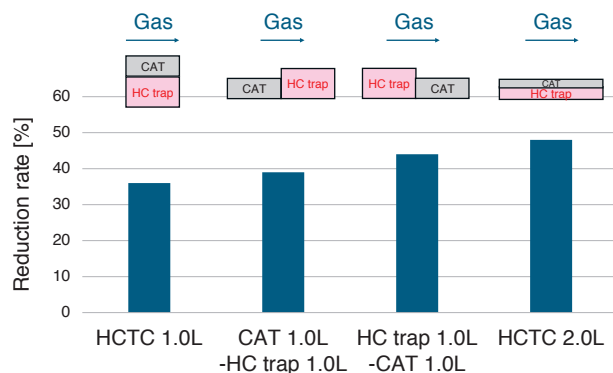


Fig. 20 Relative reduction rate of various arrangement and volume HCTC with V6 engine

used the same HC purification catalyst layer and HC trap layer coating amounts. First, at a volume of 1.0 L and an arrangement with the HC trap layer in the lower layer and the HC purification catalyst layer in the upper layer, a 36% reduction in emissions was observed compared to the TWC alone. Furthermore, arrangements with the HC purification catalyst on the front side and the HC trap materials on the rear side (1.0 L volume each) and vice versa were examined with the objective of lowering the impact of each coat on gas diffusion, and showed reductions of 39% and 44%, respectively. In particular, the latter showed an 8% reduction compared to the vertical arrangement, suggesting that a front and rear arrangement can effectively lessen the impact on diffusion. Furthermore, the arrangement with the HC purification catalyst and HC trap materials arranged vertically on a 2.0 L honeycomb provided the highest reduction effect of 48%. This is considered to be the contribution of the effect to lower the linear velocity because the larger volume resulted in thinner coats, and the effect that the greater length in the gas flow direction had on easing the adsorption and purification conditions.

5.3. Demonstration of HC Trap System Effects

An actual engine was used to verify the purification scheme of an exhaust system with an underfloor 2.0 L HCTC, which provided the best purification performance based on the above examinations of trap materials, trap catalysts, and arrangement. As a result, Fig. 21 shows that total NMOG emissions were reduced by 48% compared to the emissions using only TWC, and the profile over time in Fig. 22 exhibits a large early reduction effect as intended. As it was previously reported⁽¹²⁾ that adding an underfloor HCTC to a close-coupled 2-bed TWC arrangement in a 1.5 L turbocharged engine achieved reduction effects of 51%, the reduction effects of an underfloor HCTC arrangement have now been demonstrated in multiple engines.

These results showed that an emission reduction rate of around 50% could be achieved during the period from 0 to 300 seconds in either engine, and demonstrated the effectiveness of the HC trap concept in this study from materials to system.

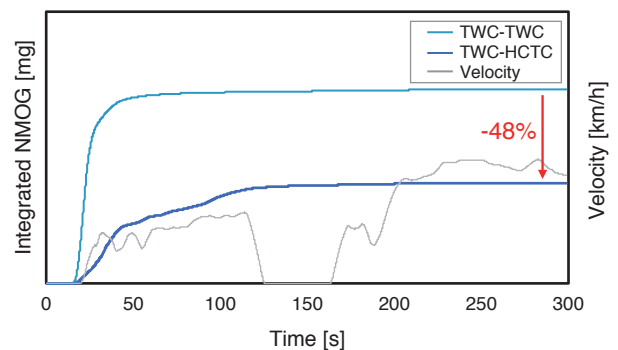


Fig. 21 Comparison of emissions between TWC and final HCTC system with V6 engine

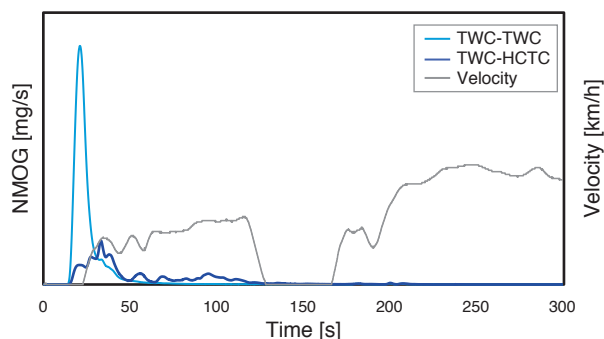


Fig. 22 Changes in HC emission profile over time using final HC trap system in V6 engine

6. Conclusion

Research on an HC trap system with high reduction effects revealed the following.

- (1) Increased stability of the exchanged ions that promote chemisorption is key to adsorbing HC up to high temperatures. Use of CHA zeolite with Ag ions introduced for the small-molecule HC trap and FAU zeolite with Cu ions introduced for the large-molecule HC trap enables increasing the adsorption and retention temperature to around 200°C.
- (2) Use of OSC material consisting of CeO₂ and ZrO₂ in a 1:1 ratio enables purification of the desorbed HC even under TWC stoichiometric conditions.
- (3) The greatest HC purification performance can be achieved by positioning a TWC catalyst containing OSC material in the uppermost layer as a catalyst for purification of trapped HC, Cu-FAU in the middle layer, and Ag-CHA in the lowermost layer.
- (4) An underfloor HCTC arrangement is highly effective not only in an L4 engine but also in a V6 engine, and reduced NMOG by 48% in the LA#4 mode test.

Reference

- (1) Rood, S., Eslava, S., Manigrasso, A., Bannister, C.: Recent advances in gasoline three-way catalyst formulation: A review, *Journal of Automobile Engineering*, Vol. 234, Issue 4, p. 936-949 (2020), doi: 10.1177/0954407019859822
- (2) Hashimoto, M., Nakanishi, Y., Koyama, H., Inose, S., Takeori, H., Watanabe, T., Narishige, T., Okayama, T., Suehiro, Y.: Development of Low Temperature Active Material for Three Way Catalyst, SAE 2016 World Congress and Exhibition, SAE Technical Paper 2016-01-0932, (2016), doi: 10.4271/2016-01-0932
- (3) Bartley, G. J.: Identifying Limiters to Low Temperature Catalyst Activity, SAE 2015 World Congress & Exhibition, SAE Technical Paper 2015-01-1025, (2015), doi: 10.4271/2015-01-1025
- (4) Williamson, W., Dou, D., Robota, H.: Dual-Catalyst Underfloor LEV/ULEV Strategies for Effective Precious Metal Management, SAE Technical Paper 1999-01-0776, (1999), doi: 10.4271/1999-01-0776
- (5) Hofstetter, J., Boucharel, P., Atzler, F., Wachtmeister, G.: Fuel Consumption and Emission Reduction for Hybrid Electric Vehicles with Electrically Heated Catalyst, SAE Int. J. Adv. & Curr. Prac. in Mobility, Vol. 3, Issue 1, p. 702-714, (2021), doi: 10.4271/2020-37-0017
- (6) Takamitsu, Y., Ariga, K., Yoshida, S., Ogawa, H., Sano, T.: Adsorption of Toluene on Alkali Metal Ion-Exchanged ZSM-5 and β -Zeolites under Humid Conditions, *Bulletin of the Chemical Society of Japan*, Volume 85, Issue 8, p. 869-876, (2012), doi: 10.1246/bcsj.20120036
- (7) Kobatake, Y., Momma, K., Elangovan, S. P., Itabashi, K., Okubo, T., Ogura, M.: "Super Hydrocarbon Reformer Trap" for the Complete Oxidation of Toluene Using Iron-Exchanged β -Zeolite with a Low Silicon/Aluminum Ratio, *ChemCatChem*, Vol. 8, Issue 15, p. 2516-2524, (2016), doi: 10.1002/cctc.201600550
- (8) Endo, Y., Nishikawa, J., Iwakura, H., Inamura, M., Wakabayashi, T., Nakahara, Y., Ogasawara, M., Kato, S.: Development of Highly Durable Zeolite as Hydrocarbon Trap Materials for Automobile Catalyst, SAE Technical Paper 2018-01-0947, (2018), doi: 10.4271/2018-01-0947
- (9) Lupescu, J., Xu, L., Jen, H., Harwell, A., Nunan, J., Alltizer, C., Denison, G.: A New Catalyzed HC Trap Technology that Enhances the Conversion of Gasoline Fuel Cold-Start Emissions, SAE Int. J. Fuels Lubr., Vol. 11, Issue 4, p. 411-425, (2018), doi: 10.4271/2018-01-0938
- (10) Nakao, K., Mitsuhashi, R., Asakawa, T.: Vehicle Emission Control Technology Utilizing Zeolite Adsorption Function, TOSOH Research & Technology Review, Vol. 63, p. 19-25, (2019) (in Japanese), <https://www.tosoh.co.jp/technology/assets/19-2-3.pdf>, (accessed 2024/11/5)
- (11) Yamamoto, S., Takaya, M., Matsushita, K.: Hydrocarbon-Adsorption Type Three-Way-Catalyst System for Reducing Cold-Start Hydrocarbon Emissions, NIPPON KAGAKU KAISHI, Vol. 2001, Issue 6, p. 333-343, (2001) (in Japanese), doi: 10.1246/nikkashi.2001.333
- (12) Takeori, H., Nemoto, K., Oku, Y., Ikutomo, R., Mori, T., Nakao, K., Usui, T., Mitsuhashi, R., Nakazawa, N., Matsuo, Y.: Study of HC Trap System to Reduce HC Emissions during Engine Cold-Start, 2024 JSAE Annual Congress (Spring), No. 17-24, 20245072, (2024)
- (13) Takahashi, H., Ishizuka, Y., Tomita, M., Nishizawa, K.: Engine-Out and Tail-Pipe Emission Reduction Technologies of V-6 LEVs, SAE Technical Paper 980674, (1998), doi: 10.4271/980674

- (14) Mitsuishi, S., Mori, K., Nishizawa, K., Yamamoto, S.: Emission Reduction Technologies for Turbocharged Engines, SAE Technical Paper 1999-01-3629, (1999), doi: 10.4271/1999-01-3629
- (15) Miyamoto, K., Tanada, H., Yamashita, M., Tanabe, K.: Development Of Technology for 3.0 L V6 Super Low Emission Vehicle, Transactions of Society of Automotive Engineers of Japan, Vol. 39, Issue 4, p. 4_65-4_71, (2008) (in Japanese), doi: 10.11351/jsaeronbun.39.4_65
- (16) Database of Zeolite Structures: <http://www.iza-structure.org/databases/>, (accessed 2024/11/5)
- (17) Liu, X., Lampert, J. K., Arendarskii, D. A., Farrauto, R.: FT-IR spectroscopic studies of hydrocarbon trapping in Ag⁺-ZSM-5 for gasoline engines under cold-start conditions, Applied Catalysis B: Environmental, Vol. 35, Issue 2, p. 125-136, (2001), doi: 10.1016/S0926-3373(01)00247-8
- (18) Kyriakidou, E. A., Lee, J., Choi, J-S., Lance, M., Toops, T. J.: A comparative study of silver- and palladium- exchanged zeolites in propylene and nitrogen oxide adsorption and desorption for cold-start applications, Catalysis Today, Vol. 360, p. 220-233, (2021), doi: 10.1016/j.cattod.2020.05.019
- (19) Takeori, H., Oku, Y., Ikutomo, R., Mori, T., Nemoto, K., Matsuo, Y., Nakao, K., Usui, T., Mitsuhashi, R., Nakazawa, N., et al.: Adsorption effect of Ag-CHA on small olefins and its application to HC Trap, 133th CATSJ Meeting Proceedings, 1P28, (2024) (in Japanese)
- (20) Oku, Y., Takeori, H., Ikutomo, R., Mori, T., Nemoto, Y., Matsuo, Y., Nakao, K., Usui, T., Mitsuhashi, R., Nakazawa, N., et al.: High-temperature adsorption effect of Cu-FAU for HC trap, 133th CATSJ Meeting Proceedings, 1P29, (2024) (in Japanese)
- (21) Usui, T., Liu, Z., Igarashi, H., Sasaki, Y., Shiramata, Y., Yamada, H., Ohara, K., Kusamoto, T., Wakihara, T.: Identifying the Factors Governing the Early-Stage Degradation of Cu-Chabazite Zeolite for NH₃-SCR, ACS Omega, Vol. 4, Issue 2, p. 3653-3659, (2019), doi: 10.1021/acsomega.8b03409
- (22) Xu, R., Wang, Z., Liu, N., Dai, C., Zhang, J., Chen, B.: Understanding Zn Functions on Hydrothermal Stability in a One-Pot-Synthesized Cu&Zn-SSZ-13 Catalyst for NH₃ Selective Catalytic Reduction, ACS Catalysis, Vol. 10, Issue 11, p. 6197-6212, (2020), doi: 10.1021/acscatal.0c01063
- (23) Yamada, T., Ashizawa, H., Nagata, M.: Multiple Regression Analysis of OSC Characteristics under Transient TWC Conditions, SAE Technical Paper 2008-01-0713, (2008), doi: 10.4271/2008-01-0713

■ Author ■



Hiroki TAKEORI



Koji NEMOTO



Yuki OKU



Ryohei IKUTOMO



Keita NAKAO



Toyohiro USUI