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Development of hydrocarbon adsorbents, oxygen storage materials for three-way catalysts and NO_x storage-reduction catalyst

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Abstract

Hydrocarbon adsorbents, three-way catalysts and NO_x storage-reduction catalysts for application in gasoline engines have been studied at Toyota in order to meet more stringent environmental regulations.

The hydrocarbon adsorption capacity of zeolites has been studied. Hydrocarbon adsorption increased with decreasing aluminum content. Zeolites with a pore size approximately 0.1 nm greater than the diameter of the hydrocarbon molecules showed the best performance. Two zeolites with different pore size were mixed, and this strategy succeeded in adsorbing hydrocarbons of carbon number 3 and above. Silver (Ag) ion-exchanged zeolite was used to increase the adsorption of exhaust gas hydrocarbons, including those of carbon number 2.

To optimize the performance of three-way catalysts, another development project focused on the heat resistance of CeO_2–ZrO_2 solid solutions (CZ) with oxygen storage capacity (OSC). We devised a new method of inhibiting the coagulation of the primary CZ particles by placing diffusion barrier layers made of alumina among the primary CZ particles. This material is called “ACZ”. The OSC and the light-off temperature of the ACZ-added catalyst are improved.

For the improvement of NO_x storage-reduction catalysts (NSR catalysts), we focused on the performance deterioration at high temperature via sulfur-poisoning and thermal degradation. A new zirconia–titania complex metal oxide was developed which improves the high-temperature performance and to promotes desorption of sulfur from the supports after aging.

Keywords: Three-way catalysts; Oxygen storage materials; Hydrocarbon adsorbents; Zeolites; NO_x catalysts

1. Introduction

With increasing interest in global environmental protection, the social demand for cleaner emissions and lower fuel consumption has been growing worldwide. In California, USA, in particular, where emissions must meet the unprecedentedly stringent low emission vehicle (LEV) II standard, the industry is required to substantially reduce emissions of hydrocarbons (HC) and nitrogen oxides (NO_x). It is therefore necessary to enhance the performance of three-way catalysts. In particular, a high-performance catalyst that can purify exhaust gases even at low temperatures has to be developed. Conventional measures to cope with the regulations consisted in enhancing the performance of catalysts and improving the engine [1]. However, these approaches are insufficient to meet the recent SULEV and PZEV regulations. Present gasoline engines decrease HC and NO_x emissions mainly by using three-way catalysts. However, 70% of the total HC emission in the driving mode (LA#4) is emitted during the first 100 s, during the “cold start” phase before engine and catalyst are warmed up. It is necessary to be able to adsorb HCs at a temperature below the catalyst’s activation level and then purify them with three-way catalysts as they desorb with increasing temperature.

NO_x is emitted almost constantly during driving. Detailed study of NO_x emission behavior during the LA#4 driving mode shows that NO_x emission increases during acceleration when the air/fuel ratio (A/F) fluctuates. This emission increase is due to the decreased NO_x conversion efficiency of the catalyst at a point where the A/F is out of the stoichiometric ratio. A solution to this problem, therefore, requires a catalyst that can maintain a high NO_x conversion performance even when A/F changes widely. The conventional three-way catalyst suppresses A/F fluctuation by using ceria (CeO_2) that provides oxygen storage capacity (OSC). With attention on the thermal resistance of ceria, development has been carried out to improve the ceria to further

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enhance the NO_x conversion performance of the three-way catalyst.

On the other hand, sharp improvements in automobile CO_2 emissions reduction (fuel economy) and exhaust gas purification have been demanded in an effort to help protect the global environment. To improve the fuel economy of the gasoline engine, a lean-burn system is being adopted as an effective technology. This trend has spurred the development of the D-4 direct gasoline injection engine for vehicles. In 1994, a new catalyst, based on a novel NO_x-purifying mechanism, was developed. NO_x is stored and held in a NO_x storage-reduction catalyst (NSR catalyst) as nitrate during lean air–fuel ratio operation. It is then desorbed from the catalyst and reduced to nitrogen under stoichiometric air–fuel conditions [2,3]. Sulfur-poisoning and heat deterioration are the main causes of deactivation of the NSR catalyst [4–6].

In this paper, recent studies at Toyota to solve these problems are described.

2. Experimental

Basic testing was performed with a packed bed reactor. A variety of HC adsorbents were prepared in the form of pellets 0.5–1.7 mm in diameter. Typically, 2.0 g of catalyst were loaded in the reactor. The gas flow rate was 10 dm^3/min. Water vapor is added to the reactor by a water vaporizer. To determine the amount of hydrocarbons adsorbed, gas containing 3000 ppmc of HC was passed through the apparatus at room temperature, and the HC concentrations of the inlet and outlet gases were measured. In engine bench evaluations, a 0.7 dm^3 monolithic adsorbent was mounted to a 2.3 dm^3 engine. The monoliths (0.7 dm^3 with 400 cells/in.^{2}) were prepared with washcoats of ZSM5 and Y-type. In some cases, ferrierite was used. The coat volume to monolithic is 200 g/dm^3. The performance of the adsorbent was evaluated 40–60 s after engine startup (first idle). The component of HC gas was analyzed by the gas chromatography. HC adsorption efficiency was determined as the ratio of inlet to outlet HC concentration.

OSC material, ACZ and CZ were synthesized by a sol–gel and a coprecipitation method. The powders were loaded to 1 wt.% of Pt by impregnation with $Pt(NO_2)_2(NH_3)_2$ in a dilute nitric acid solution, and pelletized into 0.5–1.7 mm diameter pellets. Monolith-type catalysts coated with ACZ or CZ were also prepared for a durability test using real exhaust gas at a temperature of 950 °C for 100 h. Both ACZ-added catalyst (ACZ-catalyst) and CZ-added catalyst (CZ-catalyst) were loaded with Pt and Rh by impregnation. ACZ- and CZ-catalysts were prepared on 400 cells/in.^{2} ceramic monoliths. In engine bench evaluations, a 1.3 dm^3 catalyst was mounted on a 3.0 l engine. The measurement of the catalytic activity was done with light-off test. CZ-catalyst contains alumina powder whose amount was adjusted as both catalysts have the same composition. SEM observation and oxygen storage capacity measurement were done after a thermal durability test for 10 h at 1000 °C. The SEM observation was done on polish sections with backscattered electrons image. Crystallite size of CeO_2–ZrO_2 solid solution in CZ and ACZ were calculated from the half width of XRD lines with Scherrer's equation.

All NO_x catalysts were prepared on 400 cells/in.^{2} ceramic monoliths (hexagonal cell monolithic substrate) or 0.5–1.7 mm diameter pellets. Metal oxides were used as a catalyst support. Platinum, rhodium, alkaline metals, alkaline-earth metals and rare earth elements were loaded on these supports. After drying the catalysts overnight at 120 °C, they were calcined in a flow of air. Temperature programmed desorption (TPD) of the NO desorption was detected with a Q-Mass quadrupole mass spectrometer under an inert atmosphere. In engine bench evaluations, a 1.3 dm^3 monolithic catalyst was mounted onto a 2.0 dm^3 D-4 engine. The sulfur aging test, using simulated exhaust gas, was carried out with a packed bed flow reactor. Two gas mixtures were prepared to simulate the exhaust of lean combustion (A/F $= 22$) and that of a rich air fuel ratio (A/F $= 12$), both with a high sulfur concentration (SO_2: 200 ppm). The mixtures were passed through the catalyst bed, exposing it cyclically to 55 s "lean" gas, followed by 5 s "rich" mixture. Sulfur desorption, using simulated exhaust gas, was also carried out in the packed bed flow reactor and detected with a SO_x analyzer under a reducing atmosphere.

3. Results and discussion

3.1. Hydrocarbon adsorbents

Fig. 1 shows a typical hydrocarbon adsorber and catalyst system. The system will temporarily adsorb HCs that form just after engine startup. Immediately after engine startup, the direct access valve is closed, and the gas flows into the catalyst only via the adsorbent. The valve is opened to allow purification of the desorbed HCs once the catalyst, located upstream of the HC adsorber, reaches activation temperature [7].

HCs in exhaust gases comprise paraffins, olefins, and aromatics. Each of these components contains HCs of various

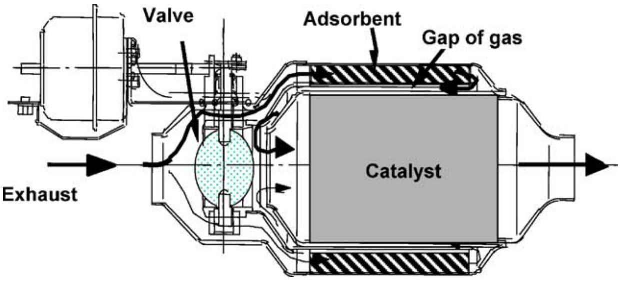


Fig. 1. A typical hydrocarbon adsorber and catalyst system.

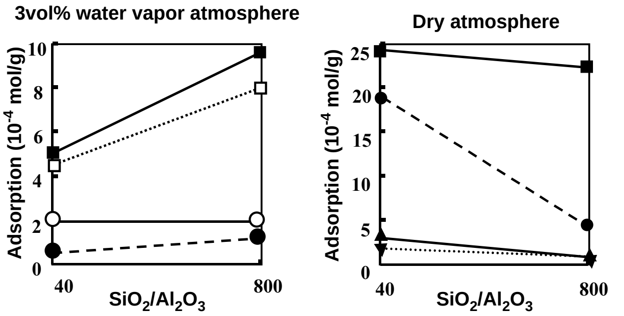


Fig. 2. The effect of Al content on HC adsorption by ZSM5 (model gas). Pellets: 0.5–1.7 mm in diameter. HC: 3000 ppm. Gas flow rate is 10 dm^3/min and absorbent weight is 2.0 g. HC: (■) $C_6H_5CH_3$; (□) n-C_8H_{18}; (○) iC_8H_{18}; (●) C_3H_6; (▲) C_2H_4; (▼) C_2H_6.

molecular weight, ranging from C1 to C11. Effective HC adsorbents must adsorb all these HC sizes. Currently, there are several adsorbents, such as active carbon and zeolite, available. For this study, zeolite was selected due to its excellent heat resistance.

Zeolites are crystalline porous SiO_2 [8]. They occur in various types, including ferrierite, ZSM5, mordenite and Y-type. Zeolites exhibit physical adsorption properties in which HCs are trapped within the zeolite pores [9]. They also exhibit chemical adsorption capabilities [10,11] at points of unbalanced electric charges resulting from the addition of Al, which can bond the HCs. Factors affecting the HC adsorption, such as pore size, water content and Al quantity, were all studied.

To study the effect of water content, the C3 adsorption rates of ZSM5 were compared in the dry state and in a 3 vol.% water vapor atmosphere. It is known that olefins are preferably adsorbed into zeolites. Adsorption was found to be considerably reduced when water vapor was present, and adsorption of olefin and paraffin were at the same levels. Though olefin is known to adsorb onto the Al sites, adsorption on Al did not occur in the presence of water vapor.

Fig. 2 shows the change in adsorption capacity of ZSM5 with Al content. HC adsorption increases with increasing Al content in dry atmosphere, but increases with decreasing Al content in the presence of water vapor. This tendency was also observed with mordenite and Y-type zeolites of different pore sizes. These results suggest that, in the absence of H_2O, HCs adsorb on the Al section, while if H_2O is present, it displaces the HC from the Al adsorption sites. Because automobile exhaust gas contains substantial amounts of water, Al-free zeolites were selected for investigation as a potential exhaust gas purifier. All discussions reported hereafter refer to analyses carried out in a water vapor atmosphere.

The effect of HC size and zeolite pore size on adsorption was studied, using C_3H_6 and $C_6H_5CH_3$ gases, which occur in large quantities within 1 min after engine startup. The results are shown in Fig. 3. The figure shows that zeolites of any pore size adsorb HCs, and that maximum adsorption is found when the pore diameter is approximately 0.1 nm greater than the diameter of the HC molecule.

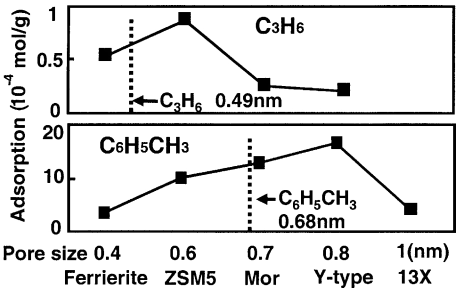


Fig. 3. The effect of zeolite pore size. Pellets: 0.5–1.7 mm in diameter. HC: 3000 ppm. Gas flow rate is 10 dm^3/min and absorbent weight is 2.0 g.

The adsorption rate of various engine exhaust gas HCs was studied using ZSM5 and Y-type zeolites. The results are shown in Fig. 4. ZSM5 was found to be inferior to the Y-type for adsorbing C8 paraffins, C7 aromatics, and other higher HCs. The Y-type, on the other hand, could not adsorb C3 olefins. These results show that ZSM5 is effective for lower (C3–C5) HCs, and Y-type is effective for higher (C6 and above) HCs. Neither adsorbent is effective for C2 and lower.

To examine the heat resistance of zeolite, HC adsorption rates were measured after varied heat treatments in 10% water vapor. Adsorption did not decrease for either ZSM5 (SiO_2:Al_2O_3 = 1800) or Y-type (SiO_2:Al_2O_3 = 400) samples treated up to 1100 °C. This confirms that both ZSM5 and Y-type will resist the heat of automobile exhaust gas.

C_2H_4, which is a C2 olefin occurring in relatively large quantities in exhaust gases, is barely adsorbed by ZSM5. This is because the molecules are too small.

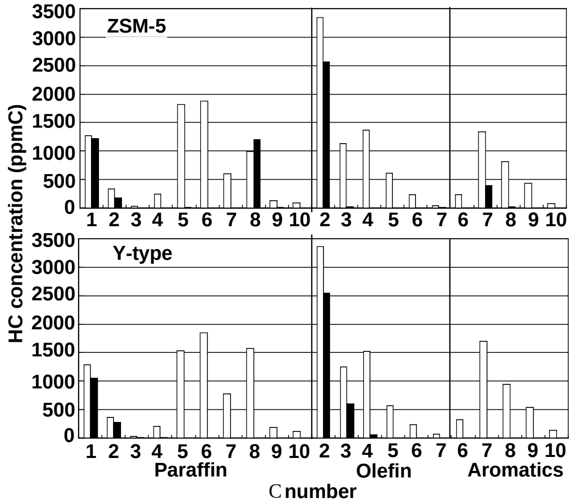


Fig. 4. HC adsorption by zeolite in exhaust gas during engine startup (first idle: 60 s). The 7 dm^3 with 400 cells/in.^{2} monolithic adsorbent was mounted to a 2.3 dm^3 engine. Washcoat volume of ZSM5 and Y-type to monolith is 200 g/dm^3. (□) Inlet gas; (■) outlet gas.

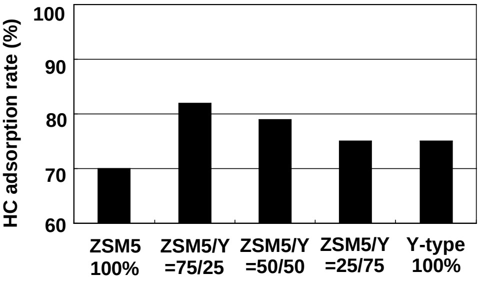


Fig. 5. ZSM5 and Y-type combined study during engine startup (first idle: 60 s). Same test conditions as in Fig. 4.

Ferrierite was also evaluated as a C_2H_4 adsorbent. This is a zeolite structure with ion-exchange sites and 0.4 nm pore size. Ion-exchanged Ag, on the Al sites of the zeolite, was found to be particularly thermally stable in ferrierite-type zeolite. The Ag loading was determined to 3×10^{-4} mol/g for the ferrierite used in this investigation. This quantity agrees with the concentration of adsorbed C_2H_4, thus confirming that ethylene is indeed adsorbed in a 1:1 ratio by Ag ions exchanged on the Al sites.

HC adsorption for mixtures of ZSM5 and Y-type was measured in order to optimize the mixing ratio. The highest adsorption was recorded for a mixing ratio of 3:1 (Fig. 5). The adsorption did not decrease when the engine exhaust temperature reached 800 °C or after 100 h durability testing. To adsorb C2 olefin that cannot be adsorbed by a ZSM5 and Y mixture, a three-component adsorbent, containing in addition Ag-ion exchanged ferrierite, was evaluated. The addition of Ag enabled C2 adsorption. This improved adsorption rate was confirmed using actual vehicle evaluations. The adsorption rate did not fall when the temperature of the adsorbents reached 500 °C (the maximum adsorption cylinder durability test temperature) or after 100 h durability testing (Fig. 6).

In May 2000, the ZSM5 + Y-type zeolite adsorbent was applied in HC adsorbing cylinders in the US production Prius (gasoline-electric hybrid vehicle) to meet the SULEV regulation.

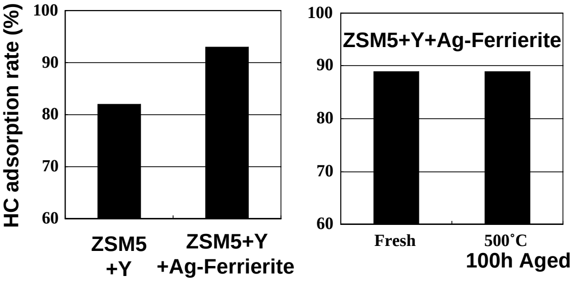


Fig. 6. Effect of adding Ag zeolite on HC adsorption. Same test condition as Fig. 4.

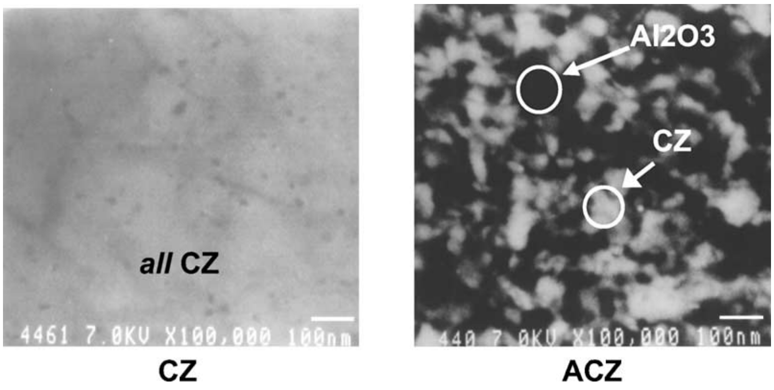
3.2. Oxygen storage materials for three-way catalysts

On the catalyst surface, the ceria keeps the ambient atmosphere stoichiometric, thereby reducing NO_x emissions. Deterioration analysis was carried out on the conventional ceria–zirconia (CZ) promoter. CZ is a solid solution in which zirconia is mixed in ceria to increase the OSC [12,13]. If the smaller Zr ion is substituted for the larger Ce ion, the gap between oxygen and the metal ion increases, and oxygen becomes easier to move in the crystal lattice.

After the high-temperature durability test, both the specific surface and the OSC decreased substantially. Conventional CZ is a collection of single-component particles. As the temperature increases, primary particles grow in size due to thermal sintering, resulting in smaller specific surface area (SSA) and lower performance as promoter. As strategy for suppressing this particle growth, we adopted the concept of arranging particles of a stable substance among primary CZ particles. Al_2O_3 was selected as the stable substance, since it is believed to non-reactive with respect to CZ. The resulting promoter/support is called “ACZ” [14–16].

ACZ and conventional CZ were subjected to 10 h durability test at 900–1200 °C in air, and the specific surface areas were measured. Even at high temperatures, the ACZ maintains a larger specific surface area than does the CZ.

Fig. 7 shows SEM photographs of polished cross-sections of CZ and ACZ powder after a 5 h durability test at 1000 °C



CZ ACZ

Fig. 7. SEM images after aging test (cross-sections of CZ and ACZ powder). Reflected electronic image. The darker parts are alumina while the brighter parts represent CZ.

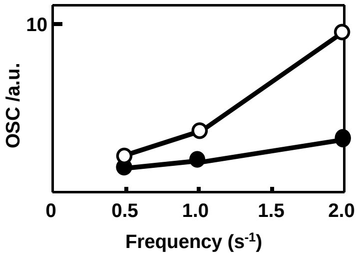


Fig. 8. OSC after durability test using engine: 62 cells/cm^2 ceramic monoliths. The 1.3 dm^3 catalyst was mounted on a 3.0 dm^3 engine. With the A/F of inlet gas varied widely from rich to lean condition, A/F fluctuation was measured at the catalyst outlet. The vertical axis is the reciprocal of A/F fluctuation at the catalyst outlet. (○) Developed catalyst (ACZ added); (●) conventional catalyst (CZ).

in air. The darker parts are alumina and the brighter parts represent CZ. CeO_2–ZrO_2 solid solution particles exist as large crystals in CZ. In ACZ, on the other hand, CeO_2–ZrO_2 solid solution exists as particle with sizes in the tens of nanometers dispersed in alumina, proving that the same distribution as our original concept has been obtained.

To ensure the dispersibility of the precious metals, alumina powders were mixed with the ACZ powders. The mixture was then coated over a honeycomb structure, on which platinum (Pt) and rhodium (Rh) were supported as precious metals, to obtain a honeycomb catalyst. The optimal ratio of alumina and ACZ powders was determined based on various considerations, such as required catalyst performance, structural stability (specifically, the stability of the specific surface area after the durability test), compatibility with precious metals, ease of coating on a monolithic structure, peeling after durability test, etc.

The ACZ-added catalyst and the conventional CZ-added catalyst were compared based on their OSC, in an engine test. An A/F sensor for measuring A/F fluctuation was installed upstream and downstream of the catalyst. The A/F of the inlet gas varied widely from the rich to lean condition, and the resulting A/F fluctuation was measured at the catalyst outlet. Smaller A/F fluctuation of outlet gas confirms a better capability of the catalyst to suppress A/F fluctuations, i.e., higher OSC. Measurements were taken using three different fluctuation frequencies. Thus, the dynamic OSC of the ACZ-added catalyst and CZ-added catalyst loaded with 1.5 g/l of Pt and 0.35 g/l of Rh was evaluated after a 100 h durability test. The durability test was performed on a 4.0 l engine using an aging cycle with alternating periods of rich and lean inlet gas stoichiometry. The rich condition was set at $A/F = 13.9$, and the lean condition was set at $A/F = 15.5$. The total cycle time under each rich or lean period was 700 ms. The inlet gas temperature during this aging cycle was kept at 900 °C. It is clearly evident from Fig. 8 that the developed ACZ-added catalyst provides higher OSC than the conventional CZ-added catalyst.

To verify the thermal stabilization effect of ACZ, the state of ceria was observed after a 5 h durability test with the temperature at 1000 °C in air using X-ray diffraction (XRD).

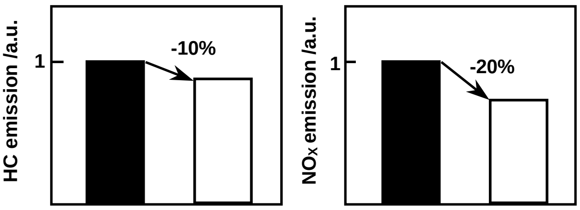


Fig. 9. Vehicle emission test (aging test: 950 °C, 100 h) 400 cells/in.^{2} ceramic monoliths. The 1.3 dm^3 catalyst was mounted on a 3.0 dm^3 engine. (☐) Developed catalyst (ACZ added); (■) conventional catalyst (CZ).

The XRD profiles of ACZ-added and CZ-added catalysts were analyzed after the durability test. For both catalysts, the qualitative analysis revealed that the ceria is present in the form of a CeO_2–ZrO_2 solid solution. After a 100 h durability test with inlet gas temperature at 900 °C on an engine, the particle size in the ACZ-added catalyst was 8.7 nm, whereas that in the CZ-added catalyst was 17.2 nm. This verifies that ACZ does prevent thermal deterioration.

This analysis also proved the effectiveness of ACZ in repressing sintering of platinum. These results verify that the synthesized ACZ can exhibit the designed performance as a promoter in a catalyst even after a durability test in an engine.

The 50% conversion temperature of the ACZ-added catalyst is about 15 °C lower than that of the CZ-added catalyst. This improvement is presumably due to the effect of repressing the sintering of platinum. Both the conventional and the newly developed catalysts were installed in actual vehicles after they had undergone the durability test, and emissions were measured. Fig. 9 shows the NO_x and HC emission measurements, respectively. The new catalyst shows superior NO_x emission reduction performance by approximately 20%, and HC emission reduction by approximately 10 %. This superiority is due to suppressed A/F fluctuation effected by the increased OSC, and due to improved conversion efficiency effected by suppression pression of platinum sintering.

3.3. Improvement of the NO_x storage-reduction catalyst

A new catalyst, based on a novel NO_x-purifying mechanism, was developed. NO_x is stored and held in a NO_x storage-reduction catalyst (NSR catalyst) as nitrate during lean air/fuel ratio operation. It is then desorbed from the catalyst and reduced to nitrogen under stoichiometric conditions (Fig. 10). Sulfur-poisoning and heat deterioration are the main causes of deactivation of the NSR catalyst. Major improvements in the durability of the catalyst were made previously to address these problems. These improvements were put into practical use in the catalyst for D-4 engines in 1996 and 1998. Additionally, the NO_x conversion performance was increased by 50% via the development of both an acidic support (TiO_2) with small particles, which effectively promotes sulfur desorption and sulfate decomposition, and a heat-resistant ZrO_2 with higher hydrogen generation per-

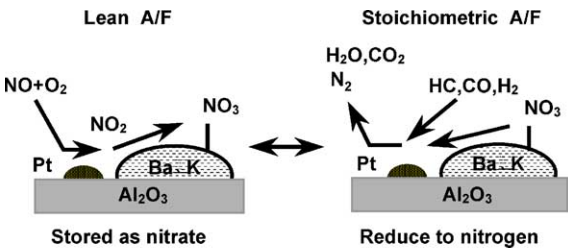


Fig. 10. NSR catalyst NO_x reduction mechanism.

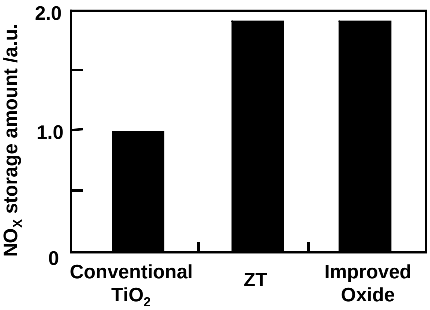


Fig. 12. NO_x storage performance. Sample: pellet catalyst (K/Pt/support). Aging condition: A/F = 22 (55 s) ↔ A/F=12 (5 s), 800 °C, 4 h. Evaluation temperature: 500 °C (inlet gas temperature).

formance. This catalyst was used as a conventional catalyst on the CROWN model beginning in October of 1999.

We know the storage characteristics of *K* contribute to the purification in the high-temperature zone above 400 °C, which is very important for the NO_x catalyst. TPD was used to observe the decomposition of KNO_3 on several supports. KNO_3 was loaded on neutral Al_2O_3, acidic TiO_2, and basic ZrO_2. Decomposition of KNO_3 was found to begin at low temperatures on TiO_2, while at higher temperatures on Al_2O_3 and ZrO_2 (Fig. 11). These findings indicate that the heat stability of KNO_3 varies depending on the supports onto which it is loaded.

The acidity of TiO_2, which promotes sulfur desorption, may reduce the heat stability of KNO_3. It was assumed that using ZrO_2 to enhancing the heat stability of KNO_3 would thus improve its performance at high temperatures.

Based on previous results, an attempt was made to compound TiO_2, which has excellent sulfur-poisoning resistance, with ZrO_2, which is effective for the thermal stability of KNO_3. This was done in order to make a KNO_3 species in which heat stability and sulfur-poisoning resistance were compatible. It is known that solid solutions from two types of support frequently show and increase in: (1) acidity of the support, (2) specific surface area, (3) heat-resistance.

The SSA is maximized when ZrO_2 is added. Following heat resistance testing, the SSA of the solid solution of TiO_2 with ZrO_2 (ZT) was 2.8 times greater than that of the physically mixed ZrO_2 and TiO_2.

ZT had doubled the high-temperature performance of the conventional TiO_2 at 500 °C after durability testing with model exhaust gas. ZT and conventional catalysts were subjected to durability testing to investigate their sulfur-poisoning behavior. The sulfur deposit on ZT was lower than that on the ZrO_2 catalyst. However, it was far higher than that of the conventional catalyst.

Next, attempts were made to control the dispersion of both the ZrO_2 and the TiO_2 in the ZT in order to improve the sulfur-poisoning resistance of each of the developed oxides. Specifically, we optimized the dispersion of TiO_2 at the surface of ZT. Thus, a new oxide was developed and evaluated. The developed oxides had much improved high-temperature performance over conventional TiO_2 at 500 °C, and about the same performance as ZT after durability testing using a model gas (Fig. 12). The SSA of the developed oxides after the heat-resistance test at 800 °C for 10 h was similar to ZT. Additionally, it was confirmed that the size of the Pt particles after the heat-resistance test at 600 °C for 10 h was smaller than that of the ZT. The effects of the developed oxides on the KNO_3 heat stability compared to the conventional TiO_2 were verified.

The catalyst developed in 1999 (conventional type), the ZT catalyst, and the newly developed catalyst using complex oxides were coated on monolithic substrate. The catalysts were then subjected to a durability test simulating urban driving. The results of the durability test indicate that the amount of sulfur deposited on the new catalyst was lower than the amount on either the conventional or the ZT catalysts (Fig. 13).

NO_x storage performance was tripled relative to the conventional catalyst by making compatible KNO_3's heat sta-

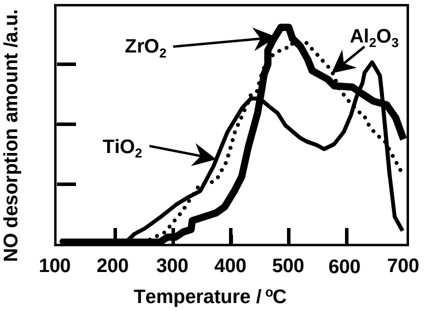


Fig. 11. TPD spectra of KNO_3. Sample: pellet catalyst (KNO_3/Pt/support). Test condition: He, 100–700 °C, analyzed by Q-Mass.

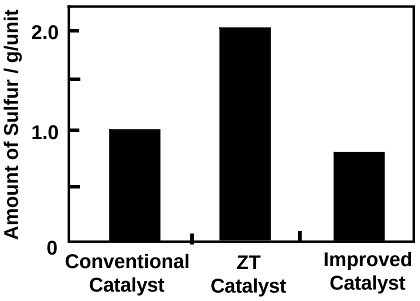


Fig. 13. Sulfur deposit amount. D-4 engine having a displacement of 2.0 dm^3 and using gasoline with high sulfur content (S: 200 ppm).

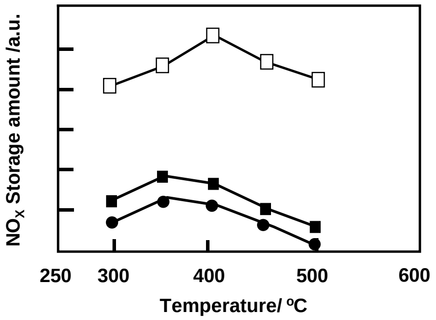


Fig. 14. NO_x storage performance (engine bench test). D-4 engine having a displacement of 2.0 dm^3 and using gasoline. (☐) Improved catalyst; (■) conventional catalyst (1999 crown model); (●) 1998 vista model.

bility and by improving the sulfur desorption behavior. Thus, the development target was achieved (Fig. 14).

The NO_x emissions in 10–15 driving mode, following the durability test drive, were about one-third that of the conventional catalyst. This confirms the drastic improvement in the durability performance of the developed catalyst, and offers the promise of possibly meeting the requirements for even higher NO_x conversion.

4. Conclusion

1. The factors for improving the physical adsorption characteristics of zeolite were identified. The effect of zeolite pore size and Al content were clarified. It is easiest to adsorb HCs of a molecular diameter that is equal to the zeolite pore size -0.1 nm. In zeolites with Al-content, the HC adsorption is much reduced in a water vapor atmosphere.
2. HC adsorbents (ZSM5 and ferrierite) containing ion-exchanged Ag, to improve chemical adsorption characteristics, are particularly thermally stable, and adsorb C2 olefin. In May 2000, the ZSM5 + Y-type zeolite adsorbent was applied in HC adsorbing cylinders in the US production Prius to meet the SULEV regulation.
3. As a measure to improve the conventional CZ promoter, alumina particles have been arranged in primary CZ particles, thereby developing a new promoter called ACZ that has the effect of suppressing thermal sintering.
4. A new, heat-resistant three-way catalyst has been developed using the developed ACZ.
5. The developed catalyst provides higher OSC and therefore higher emission reduction efficiency than the conventional catalyst.
6. This improvement in catalyst performance is due to suppressed A/F fluctuation effected by high OSC after durability testing, and due to repressed sintering of platinum.
7. A new complex oxide ZT, making the sulfur-poisoning resistance and heat stability of KNO_3 compatible, was developed. In March 2001, the NO_x catalyst was further improved based on the findings of this study. This catalyst was placed into practical application for use with D-4 engines.

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References

[1] M. Shinichi, Catal. Surv. Jpn. 1 (1997) 111–117.
[2] N. Miyoshi, S. Matsumoto, K. Katoh, T. Tanaka, J. Harada, N. Takahashi, K. Yokota, M. Sugiura, K. Kasahara, SAE Paper 950809, 1995.
[3] K. Kato, T. Kihara, T. Asanuma, M. Goto, N. Sibagaki, TOYOTA Tech. Rev. 44 (2) (1994) 27.
[4] H. Suzuki, M. Riemi, T. Naoki, TOYOTA Tech. Rev. 46 (2) (1996) 68.
[5] Y. Ikeda, K. Sobue, S. Tsuji, S. Matsumoto, SAE Paper 991279, 1999.
[6] I. Hachisuka, H. Hirata, Y. Ikeda, S. Matsumoto, SAE Paper 2001-01-1196, 2000.
[7] T. Kanazawa, K. Sakurai, SAE Paper 2001-01-0660, 2001.
[8] Y. Takeuchi, Adsorption Technology Handbook, P643, NTS, 1999.
[9] S. Namba, T. Yashima, Zeolites 4 (1984) 77.
[10] H. Herden, W.D. Einicke, M. Jusec, U. Messow, R. Scrollner, J. Colloid Int. Sci. 97 (1984) 559.
[11] N.Y. Chen, J. Phys. Chem. 80 (1997) 64.
[12] M. Sugiura, A. Suda, Y. Nagai, T. Suzuki, H. Sobukawa, in: Proceedings of the 88th Meeting of the Catalyst Society of Japan, Oita, October 2001, Abstract no. 3 D25.
[13] H. Sobukawa, A. Suda, Y. Ukyo, T. Suguki, M. Kimura, M. Sugiura, Y. Ikeda, H. Hirayama, Catalyst 43 (2001) 107, No. 87 Catalyst Symposium 2A13.
[14] T. Kanazawa, J. Suzuki, T. Takada, T. Suzuki, A. Morikawa, A. Suda, H. Sobukawa, M. Sugiura, SAE Paper 2003-01-0811, 2003.
[15] T. Suzuki, A. Morikawa, A. Suda, M. Kimura, H. Sobukawa, M. Sugiura, T. Kanazawa, S. Matumoto, in: Proceedings of the 88th Meeting of the Catalyst Society of Japan, Oita, October 2001, Abstract no. 3A08.
[16] T. Kanazawa, J. Suzuki, T. Takada, T. Suzuki, A. Morikawa, A. Suda, H. Sobukawa, M. Sugiura, in: Proceedings of the 88th Meeting of the Catalyst Society of Japan, Oita, October 2001, Abstract no. 3A09.