Transactions of the Materials Research Society of Japan 24 [3] 373-377 (1999)

Stringent Emission Regulation Trends and Recent Technologies of Autoexhaust Catalyst

Teiji Yamada, Takeshi Kobayashi, Katsuaki Katoh and Yukio Kosaki
N.E.Chemcat Corporation, 678 Ipponmatsu, Numazu, 410-0314, Japan
Fax: 81-559-66-1832, e-mail: necc.teiji.yamada@nifty.ne.jp

The status and improvements made in current de-NO_x catalyst under oxidizing atmosphere is summarized for both gasoline and diesel powered vehicle applications. In regards to gasoline powered applications, two types of catalyst approaches were investigated. One was a NO_x trapping and reduction type by the Pt/Rh based catalyst, the other was a selective reduction type by Ir based catalyst. As for the thermal deterioration of NO_x trapping and reduction type catalyst below 700°C, a contribution of Pt sintering was much larger than that of trapping material degradation. NO_x trapping property in oxidizing atmosphere were disappeared by sulfur treatment around 400°C. Regeneration of sulfur poisoned catalyst in reducing atmosphere above 600°C was effective for the recovery of NO_x trapping capability. In case of the selective NO_x reduction with hydrocarbons, Ir/SiC showed lower light-off and wider effective temperature window for de-NOx performances than Cu/ZSM-5 and Ir/Al_2O_3. Use of SiC support remained active Ir metal states under the oxidizing atmosphere at 500°C. Reductant sensitivity and oxygen dependency remain as major challenges for Ir de-NO_x catalyst as well as thermal stability at high temperature. As to the diesel powered application, use of Pt/ZSM-5 was effective to improve NO_x emission performances without sacrificing gas phase and particulate matter emission performances.

Key Words: Autoexhaust Emission, de-NO_x Catalyst, Pt/Rh, Ir/SiC, Pt/ZSM-5

1. INTRODUCTION

With global growing concerns on environmental issues, the development of the newest approaches for autoexhaust system has become more interesting for achieving stringent emission regulations and greenhouse gas(CO_2) reduction. As one of effective approaches to reduce the hazardous gases and CO_2, direct-injection(DI)-engines were used for both gasoline and diesel powered vehicle under the lean fuel conditions[1)2)]. Since the conventional TWC catalyst does not work well under the excessive O_2 environment, the development of a breakthrough de-NO_x catalyst became an essential task to overcome these challenges.

In this report, the improvement status and unresolved issues of current de-NO_x catalyst are summarized for both gasoline and diesel applications.

2. EMISSION REGURATION TRENDS

Since air pollution generated by automobile emission globally has become a growing concern, various regulatory measures have been introduced worldwide to minimize its potential damage on environment. Summarized below are the most severe regulation and proposal in California of U.S.A. and Europe for passenger gasoline and diesel vehicles[3)].

Table I Emission Standard of California (Gasoline)

	1993	1998(LEV)	2004(LEV-2)
NO_x	0.4	0.2	0.05
HC	0.25	0.075	0.075
CO	3.4	3.4	0.34

(Unit : g-emission per one-mile driving)

2.1 California (U.S.A.)

Table I shows the transition in California's exhaust emission standard values as non-methane organic gases (NMOG), carbon monoxide (CO) and nitric oxides (NO_x) in each of the categories. These emission values are evaluated after 80,000 km fleet aging and by the FTP-75 driving pattern. Since photochemical smog pollution has not been improved for past decade, NMOG and NO_x are strongly concerned.

2.2 Europe

Table II and III shows gasoline and diesel emission standards in Europe respectively after

Table II Emission Standards of Europe (Gasoline)

	1994(Euro-1)	1998(Euro-2)	2005(Euro-4)
NO_x	-	0.252	0.08
HC	-	0.341	0.1
HC+NO_x	0.97	-	-
CO	2.72	3.2	1

(Unit : g-emission per one-km driving)

Table III Emission Standard of Europe (Diesel)

	1994(Euro-1)	1998(Euro-2)	2005(Euro-4)
NO_x	-	0.63	0.25
HC+NO_x	0.97	0.71	0.30
CO	2.72	1.06	0.50
PM	0.14	0.08	0.025

(Unit : g-emission per one-km driving)

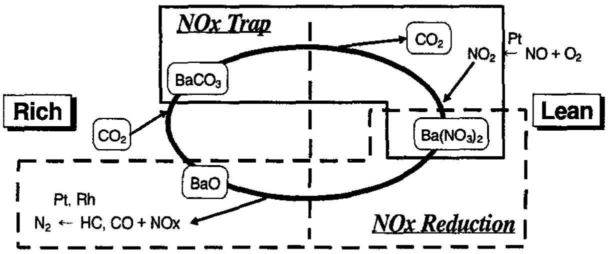

Fig.1 Proposed Reaction Mechanism of NOx Trapping-Reduction by thermodynamics approaches

European ECE/EUDC driving pattern. Both hazardous exhaust and CO_2 emission reduction are considered in Europe, while NO_x and particulate matter (PM) are strongly focused.

3. RECENT TECHNOLOGIES OF AUTOEXAUST CATALYST

3.1 NO_x Trapping and Reduction Catalyst for DI Gasoline Application

NO_x trapping-reduction catalyst application has been commercialized for lean burn and DI gasoline engine since 1994 in Japan[4]. The proposed reaction mechanism by thermodynamics approaches was shown in Fig.1[5]. In order to purify NO_x to non-hazardous N_2, the catalyst were periodically exposed to two Air/Fuel conditions by changing engine management system;

1) During the lean operation in oxidizing atmosphere,
$NO + 1/2O_2 \rightarrow NO_2$ [A]
M-carbonate + $NO_2 + O_2 \rightarrow$ M-nitrate + CO_2 [B]
2) During the rich operation in reduction atmosphere,
M-nitrate $\rightarrow$ M-oxide + NO_x [C]
NO_x + HC/CO $\rightarrow N_2 + H_2O + CO_2$ [D]
M-oxide + $CO_2 \rightarrow$ M-carbonate [E]

Table Ⅳ Cyclic Synthetic Gas Composition

	Lean (2 min.)	Rich (1 min.)
C_3H_6 (C_1 ppm)	4,500	4,500
NO (ppm)	250	250
O_2 (%)	7.5	0.5
CO (%)	0.2	0.2
CO_2 (%)	9.0	9.0
H_2O (%)	10	10
N_2	balance	balance

SV = 60,000/hr, Inlet temp. = 350℃

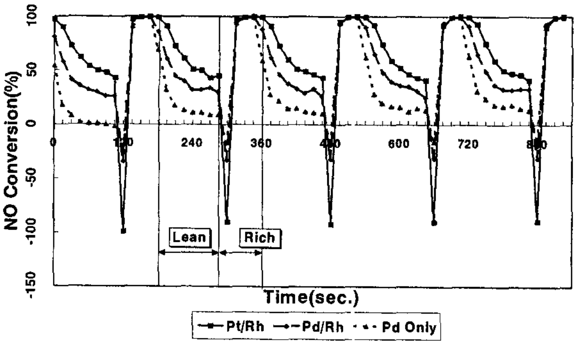

Fig.2 Effect of Precious Metal Species on Apparent NO_x Conversion at Lean

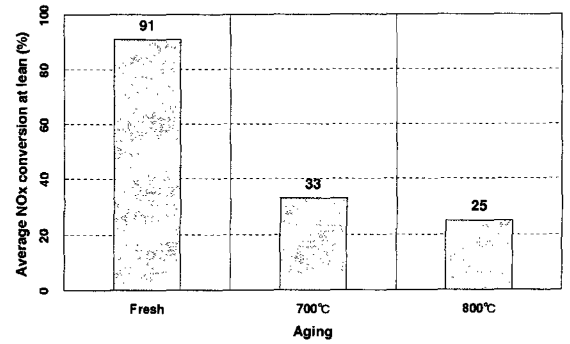

Fig.3 Effect of Thermal Aging Temperature on Apparent NO_x Conversion

As to NO_x trap reaction at lean, step [A] is strongly depended on NO oxidation activity by precious metals, while step [B] is dominated by the equilibrium of this equation. At rich, step [C] and [E] immediately occurred by the equilibrium and step [D] is the same as the catalytic reaction by conventional TWC catalyst.

Since step [A] and [B] affected the apparent NO_x conversion strongly, the influence of precious metal species was investigated. TableⅣ summarized cyclical gas conditions in synthetic gas experiments. As shown in Fig.2, the use of Pt/Rh was more effective to enhance NO_x trapping performance under lean condition than that of Pd/Rh and Pd-only. This ranking of trapping performances agreed with that of NO oxidation performances. The release of trapped NO_x during condition changes from lean to rich was also observed. This indicated that improvement of NO_x reduction performance by conventional TWC function during short period would be one of important future tasks.

As shown in Fig.3, NO_x trapping-reduction catalyst showed large thermal deterioration over 800°C. To identify failure mode, the impact of thermal deterioration on each component of $Pt/Ba/Al_2O_3$ catalysts were investigated. As shown in TableⅤ, three $Pt/Ba/Al_2O_3$ with different preparation and aging procedures were evaluated: (1) fresh, (2) use of thermal aged Ba/Al_2O_3, and, (3) use of thermal aged Pt/Al_2O_3. Fig.4 shows apparent NO_x conversion of three catalysts. Catalyst with thermally degraded Ba showed small impact by 700°C aging, whereas catalyst with thermally sintered Pt displayed significant drop in NOx conversion from 74% to 40%. These suggested that the failure mode of 800°C aged NO_x trap-reduction catalyst was at the NO oxidation step catalyzed by precious metal rather than at the nitrate formation step governed by trapping components. The maintenance of high precious metal dispersion, therefore, was recognized as

Table Ⅴ $Pt/Ba/Al_2O_3$ Catalyst Preparation Procedure
Catalysts; Pt = 1.0g/L, 62cell/cm^2,
Aging: 700℃x5hrs in 10%H_2O/Air
1) Standard : $Pt/Al_2O_3 + Ba/Al_2O_3 \rightarrow Pt/Ba/Al_2O_3$
2) Pt Sintering: $Pt/Al_2O_3 \rightarrow$ *Aging $\rightarrow Pt/Ba/Al_2O_3$
Ba/Al_2O_3 ——↑
3) NO_x Trapper : $Ba/Al_2O_3 \rightarrow$ *Aging $\rightarrow Pt/Ba/Al_2O_3$
Degradation Pt/Al_2O_3 ——↑

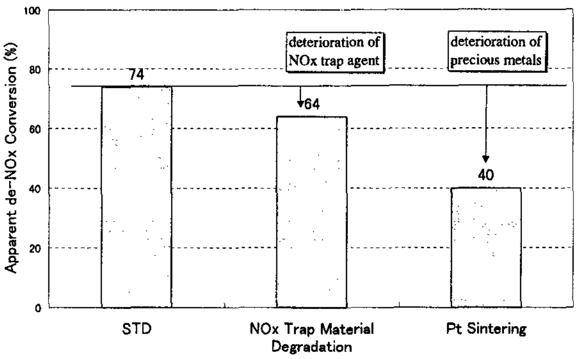

Fig.4 Effect of Failure Mode on de-NOx Performance

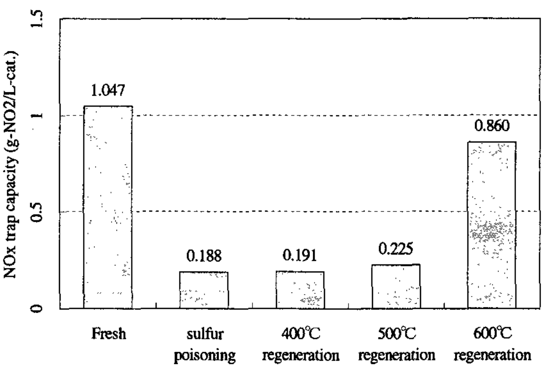

Fig.4 Effect of Failure Mode on de-NOx Performance

one of key challenge for further NO_x conversion improvements.

Catalyst degradation by sulfur is another issue of NO_x trapping-reduction type catalyst. Thermodynamics calculation implied that the equilibrium of SO_x trapping process was more realistic than that of NO_x trapping process in the actual exhaust gas. Fig.5 showed the effect of sulfur accumulation and impact of regeneration on NO_x trap capacity. This catalyst showed NO_x trapping capacity over 1.0g per 1.0 liter at fresh, while, after sulfur treatment at 400°C in oxidizing condition, the trapping capacity dropped below one-fifth of the fresh. The stored sulfur on NO_x trapping site was not easily regenerated below 500°C even in reducing condition. After 600°C regeneration, NO_x trapping capacity was recovered back up to approx. 80%. In order to broaden this application to become a global countermeasure for stringent emission standards, reduction of sulfur content in fuel is suggested to be considered in parallel with catalyst and system approach improvements.

3.2 Selective NOx Reduction Catalyst for DI Gasoline Application

Since NO_x trapping-reduction system is inhered with a risk of fuel penalty issue, approaches with simpler, passive, selective NOx reduction catalyst still remained as another area of great interest. Although many catalyst systems such as Cu-ZSM-5 and Pt/Al_2O_3 have been studied and reported[6], use of Ir as active spices was found to be effective for NO_x reduction in DI gasoline engine application.

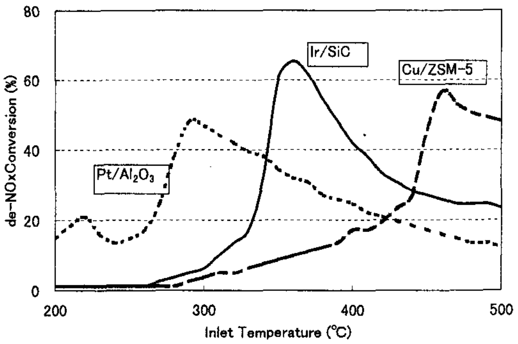

Fig.6 Comparison of de-NOx Profile among Cu/ZSM-5, Pt/Al2O3 and Ir/SiC

Table VI Effect of Support Material on de-NO_x Performances and Ir Reoxidation Behavior by TG Measurement

Support	de-NO_x Performance		IrO_2 Re- Oxidation	
Material	Max.Conv.	C-max Temp.	Start	Completion
SiC	44%	365℃	500℃	1000℃
Al_2O_3	24%	415℃	400℃	800℃

* Max. Conv.: Maximum de-NO_x Conversion
C-max Temp.: Temperature at Max. Conv.
Start: Starting Point of Ir Reoxidation by TG
Completion: Completion Point of Ir Reoxidation by TG

Fig.6 compares de-NO_x profiles among Cu/ZSM-5, Pt/Al_2O_3 and Ir/SiC. Ir/SiC showed lower de-NO_x light-off temperature and wider operating temperature window than Cu-ZSM-5. Also, Ir/SiC provided higher maximum de-NOx conversion without N_2O formation. However, Ir/SiC was inferior to Pt/Al_2O_3 in de-NO_x light-off performance. It was supposed that mild oxidation capability on Ir/SiC would result in above proper characteristics. Table VI shows the impact of support materials on de-NO_x activity of Ir based catalysts. Use of SiC was superior to that of Al_2O_3 in de-NO_x performance. Since interaction between Ir and support material could affect de-NO_x performance, Ir valance state were evaluated by TG measurement in air after reducing treatment. As shown in Table VI, Ir on Al_2O_3 easily became oxidized state around 400°C, whereas oxidation of Ir on SiC gradually commenced from 500°C. This suggested that the maintenance of Ir metal state on SiC would be the reason of its enhancement of de-NO_x performance.

However, there are many issues stayed as main challenges for Ir/SiC system. They are (1) strong influence of co-existing gases and (2) insufficient thermal stability. Table VII shows the impact of reductant HC species on de-NO_x activity; propylene (C_3H_6) vs. propane (C_3H_8). Ir/SiC showed 65% of maximum de-NO_x activity in C_3H_6 contained gas, while few activity in C_3H_8 contained gas. These suggested that intermediate species of unsaturated hydrocarbons would be only effective to react with adsorbed NO on Ir/SiC. As shown in Fig.7 and Fig.8, HC/NO_x ratio and O_2 content in exhaust gases affected de-NO_x performances of Ir/SiC catalyst. These indicated that improvements of these sensitivities were also one of key issues for actual

TableⅦ Effect of HC Species on de-NO_x Performances of Ir/SiC Catalyst

HC Species	de-NO_x Performance		Oxidation Activity at C-max Temp.	
As Reductant	Max. Conv.	C-max Temp.	HC	CO
Propylene(C_3H_6)	65%	365℃	94%	89%
Propane (C_3H_8)	9%	360℃	1%	49%

* Max.Conv.: Maximum de-NOx Conversion
C-max Temp.: Temperature at Max. de-NOx Conv.
HC, CO: HC and CO conversion at Max. de-NOx Conv.

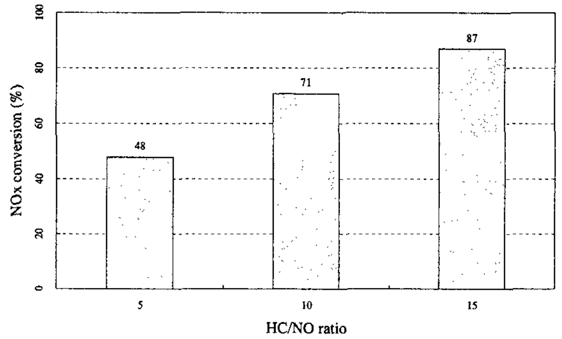

Fig.7 Effect of HC/NO_x Ratio on Maximum de-NO_x Performance of Ir/SiC Catalyst

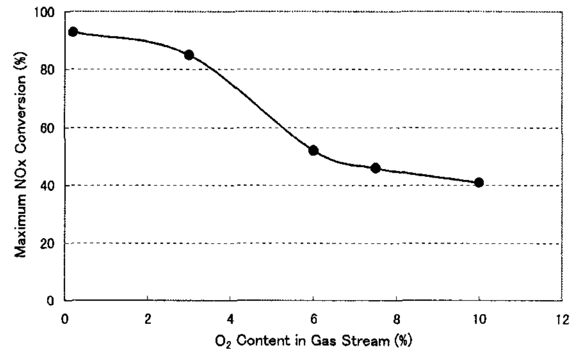

Fig.8 Effect of O_2 Content in Gas Stream on de-NOx Performance of Ir/SiC Catalyst

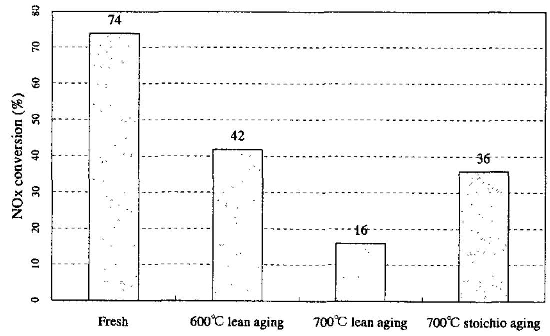

Fig.9 Effect of Aging Conditions on de-NO_x Performance of Ir/SiC Catalyst

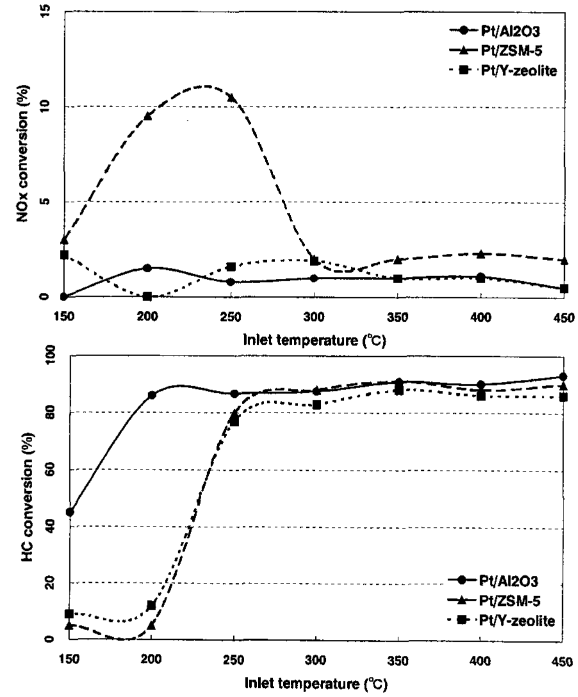

Fig.10 Passive de-NO_x and HC Oxidation Perormances of Diesel Catalysts among Pt/Al_2O_3, Pt/Y-zeolite and Pt/ZSM-5

application in the market.

Fig.9 shows de-NO_x performances of Ir/SiC catalyst after various engine aging. Maximum de-NO_x conversion of fresh Ir/SiC catalyst was 74%, whereas it dropped to 42% and 16% by 600 and 700°C lean aging respectively. A comparison of 700°C aging between stoichiometric and lean conditions suggested that oxygen partial pressure in the gas stream strongly affected Ir valence state at active sites, which resulted in different de-NO_x performance after aging. Since Ir based catalyst showed a characteristics of sulfur tolerance, thermal stability improvement of Ir based catalyst would be of further interest in future application.

3.3 NO_x Reduction for Diesel Application

Since diesel engine is superior to conventional gasoline SI engine by approx. 25% in fuel economy, diesel engine has been strongly considered as an effective way to reduce CO_2 from mobile source. However, as in the gasoline DI engine emission system, de-NO_x performance in excessive oxygen atmosphere is one of strongest concerns in diesel application[7].

Fig.10 shows passive de-NO_x and HC oxidation performances in diesel bench evaluation among Pt/Al_2O_3, Pt/Y-zeolite and Pt/ZSM-5. Pt/Al_2O_3 showed

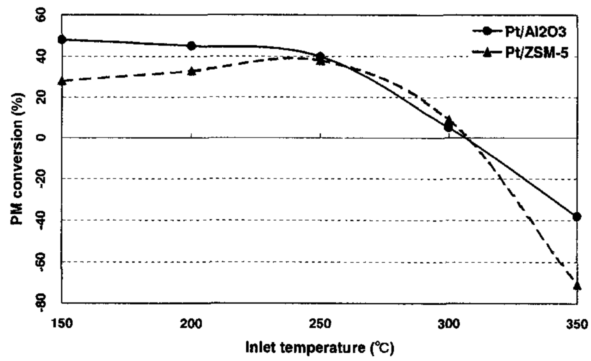

Fig.11 Comparison of Particulate Matter Reduction Between Pt/Al_2O_3 System and Pt/ZSM-5

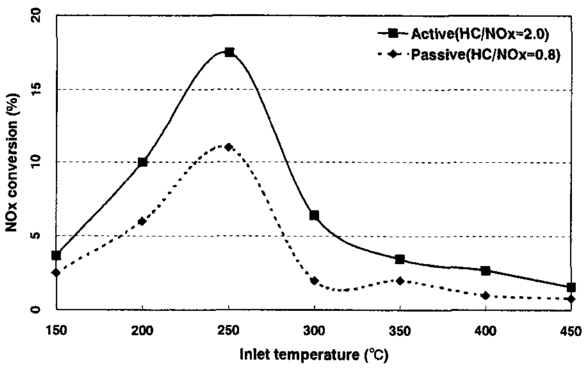

Fig.12 Effect of HC Injection on de-NOx Performance of Ir/SiC Catalyst

few % de-NO_x conversion at fresh, while Pt/ZSM-5 showed over 10% de-NO_x conversion between 200℃ and 250°C. Since there were large differences in HC oxidation activities between the two, intermediate HC species might contributed to the de-NO_x performance improvement. On the other hand, Pt/Y-zeolite did not show any de-NO_x performance even though it showed similar HC oxidation performance as Pt/ZSM-5. It implied that differences by zeolite sources in acid site quantity and/or pore structure would result in a change in HC/NOx ratio at micro-domains and/or HC reductant species for proceeding de-NO_x reaction. Fig.11 shows the performances of particulate matter reduction between Pt/Al_2O_3 based oxidation catalyst and Pt/ZSM-5 de-NO_x catalyst. Although the oxidation ability of Pt/ZSM-5 was suppressed for formation of active intermediate HC species, Pt/ZSM-5 showed similar particulate reduction as Pt/Al_2O_3 catalyst except for temperature range between 200℃ and 300℃.

Since HC/NOx ratio were less than three when many of NO_x emission were generated in the actual diesel gas stream, effect of active HC fuel injection was evaluated in engine bench. By the means of increase in HC/NO_x ratio from 0.8 at passive to >2.0 at active, de-NO_x conversion was increased from 10% to 17% as shown in Fig.12. However, since particulate matter and gas phase conversion will become another issues for HC injection, it should be essential to consider the introduction of an offset between de-NO_x performance and these other emissions.

TableⅧ Trends of Sulfur Content in European Fuel

Year	1998	2000	2005
Gasoline	300	150	50
Diesel Oil	450	350	50

(Unit: ppm Sulfur)

4. Summary

From both standpoints in domestic air quality improvement and global environmental preservation, development of autoexhaust catalyst, particularly de-NO_x catalyst, has become increasingly attractive and important. In order to achieve such dynamic challenges, however, improving circumstance regarding to the catalyst usage such as sulfur content reduction in fuel will also be vital. TableⅧ summarizes the proposal of sulfur content reduction in Europe. Sulfur beyond 2005 year will be less than one-sixth of current level in the market. Furthermore, providing enough and appropriate reductants under excess oxidizing atmosphere is another important matter. In other words, new "exhaust system development" for enhancing catalyst properties will be of equal importance to reduce overall NO_x emission as the development of de-NO_x catalyst itself.

5. References

1) M.P.Walsh: "Motor Vehicle Trends and the Implications for Emissions Regulation", Haus Der Technik E.V.: Prosperity and Environmental Protection, Essen (1998)
2) K.P.Schindler, "Status of World wide Exhaust Legislation", Haus Der Technik E.V.: Prosperity and Environmental Protection, Essen (1998)
3) P. Degobert: "Automobiles and Pollution, Chapter 6: Laws and Regulation", pp101-161, Society of Automotive Engineers, Inc. (1996)
4) N.Miyoshi , et.al., "Development of NO_x Storage-Reduction 3-Way Catalyst for Lean-Burn Engines2, Toyota Technical Review, pp24-29Vol.44, No.2 (1994)
5) K.Kobayashi, et.al., "Study of NO_x Trap Reaction by Thermodynamic Calculation", SAE Paper No.970745 (1997)
6) M.Iwamoto, et.al., "Selective Reduction of NO by Lower Hydrocarbons in the Presence of O_2 and SO_2 over Copper Ion-exchanged Zeolites", 66th CATSJ Meeting Abstracts:No.2L404, Vol.32, No.6 (1990)
7) K.Katoh, et.al., "Compatibility of NO_x and PM Abatement in Diesel Catalysts", SAE Paper No.980931 (1998)

(Received December 11, 1998; accepted March 8, 1999)