

## Recent Development Trends in Catalyst Technologies for Reducing Nitrogen Oxides Emissions

YASUSHI OZAWA

*Affiliated Fellow*

KUNIKO URASHIMA

*Environment and Energy Research Unit*

### 1 Introduction

A catalyst is an essential component in a variety of production processes including fuel refining (e.g. gasoline), synthesis of plastics (clothing, automobiles, electric apparatus, domestic products), as well as a multitude of pharmaceutical products. It plays another important role in maintaining our health by way of removal of hazardous components from the emissions of automobiles and factories. A catalyst is a chemical substance that, even in small amounts, accelerates chemical reactions and may be recovered essentially unaltered. Some catalysts show selectivity as well as rate enhancement. In the presence of same source materials, a judicious choice of catalyst can accelerate only a selected chemical reaction where others are possible. The catalytic activity of a solid surface was first discovered by the English chemist Davy in 1817, and the first industrial catalytic process was developed for low-temperature ammonia

synthesis by German chemists Haber and Bosch in 1913. A multitude of catalytic processes have since been developed<sup>[1]</sup>, and have played important roles in a range of industries and in maintaining environmental integrity (see Table 1). Catalysts may take various states and forms: some liquids, such as sulfuric acid, can show catalytic activity. Solid catalysts may be used as granules/powder, or may be used as a fine particle dispersed on a substrate or carrier made of, for example, ceramics. These hybrid systems (e.g. catalyst and carrier) may take various forms including powders, granules, fibers, plates, or honeycomb structures, depending on the nature of the chemical reaction in which the catalyst system will be used.

This article presents an overview of the current technological status regarding nitrogen oxides (NOx) emission reduction catalysts used for both mobile and fixed sources, and describes the challenges that must be addressed in future developmental efforts.

**Table 1** : Types of catalyst

Class	Application	Typical catalyst
Industrial	Petroleum refinery	Cracking, Hydrocracking, Desulfurization, Reforming catalyst
	Petrochemical product	Hydrogenation, Oxidation, Polymerization catalyst
	Pharmaceutical/Food	Hydrogenation, Oxidation, Isomerization catalyst
	Others	Natural gas reforming, Fuel cell electrode catalyst
Environmental	Vehicle emission	Three-way, PM oxidation catalyst
	Others	NOx removal, Dioxin/VOC decomposition, Deodorizing catalyst, Photocatalyst

## 2 Current situation of air pollution and NO<sub>x</sub> emissions regulation

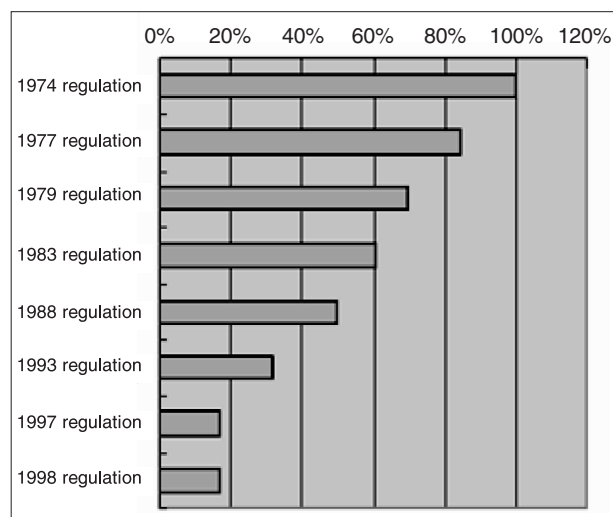
### 2-1 Current status in Japan

Various air pollutants are discharged from mobile sources such as automobiles, ships and aircraft, and from fixed sources such as factories, power plants and waste incinerators. The current situation of air pollutant concentrations in Japan has already been reported in one of the articles in this series (January 2006)<sup>[2]</sup>. According to the report, in contrast to sulfur dioxide (SO<sub>2</sub>) and carbon monoxide (CO) emissions that have been substantially reduced, nitrogen dioxide (NO<sub>2</sub>) has shown hardly any sign of improvement and photochemical oxidant concentrations (NO<sub>x</sub> is generally believed to be one of the triggering substances) have even shown an upward trend in recent years.

Brochures issued by the Ministry of the Environment and Ministry of Land, Infrastructure and Transport in 2002 ascribe NO<sub>x</sub> emission sources as 52% from automobiles and 35% from factories/offices, which clearly demonstrates the importance of addressing automobile NO<sub>x</sub> emissions. Figure 1 shows the trends in NO<sub>x</sub> emissions from heavy diesel trucks and buses. As is apparent from the chart, NO<sub>x</sub> emissions have been reduced yearly and are down to less than 20% of 1974 levels under 1988 regulation<sup>[3]</sup>.

Japan has traditionally imposed some of the most stringent regulations on NO<sub>x</sub> emissions. A typical example of these schemes is the Automobile NO<sub>x</sub> Law (enacted in 1992) for reducing air pollution caused by NO<sub>x</sub> emissions in large urban areas. The NO<sub>2</sub> air quality standard for urban areas, however, has not yet been attained, largely because of the ever-increasing number of automobiles in these areas<sup>[4]</sup>. Air pollution caused by emissions of particulate matter (PM) is also a serious problem. PM from diesel-powered automobiles is a matter of particular public concern because its components are believed to be carcinogenic. Based on these findings, the above law was revised in June 2001. The purpose of the revision was to reduce PM discharge from automobile traffic, as well as to

**Figure 1** : Trends in NO<sub>x</sub> emission reduction from diesel trucks/buses (direct injection)



(Note) Total vehicle weight: 1.7-2.5 tons

Source: "Road Pocketbook, 1999", Japan Highway Users Conference

strengthen NO<sub>x</sub> regulations. PM was added to the list of target materials in addition to NO<sub>x</sub>, and the areas to be regulated were also extended. To comply with the revised law, stepwise strengthening of the regulation on emissions from diesel automobiles has been carried out. To meet the requirements contained in these regulations, considerable effort has been undertaken towards producing higher purity fuel and enhancing the performance of engines and emission reduction catalysts<sup>[5-10]</sup>.

For fixed sources, NO<sub>x</sub> emissions are regulated by governmental ordinance, as well as additional regional regulations, depending on the type and scale of the facility. Even total volume control of NO<sub>x</sub> pollutants is enforced in selected areas. Only very small installations are exempt from these regulations. Construction of a new large facility or extension of an existing one is examined by the national/regional government in terms of its affect on the environment (environmental impact assessment). Environmental protection measures, including NO<sub>x</sub> reduction, are the key features that are examined.

### 2-2 Current status in the U.S.

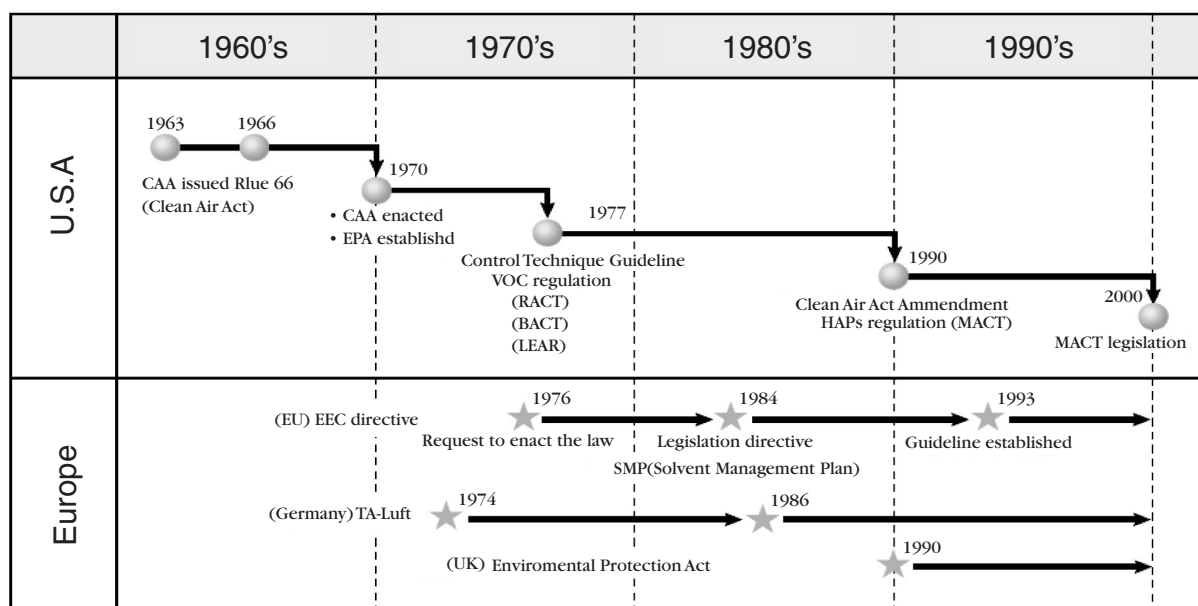
Many areas in the U.S. have not yet attained the levels specified by the atmospheric standard for ozone (main source for photochemical oxidants), PM, and CO. Automobile emissions in the U.S. make a larger contribution to atmospheric

concentrations of NO<sub>x</sub> and CO than is the case in other countries. Some efforts have been made, like Japan, to strengthen the regulations on automobile emissions and new tighter regulations are scheduled to be implemented in 2007 and beyond. European countries also have plans to implement tighter regulations (timing and contents are yet to be decided) <sup>[11]</sup>. Figure 2 summarizes the history of environmental regulations in the U.S. and Europe.

As shown in Table 2, the U.S. has implemented many regulations to counter NO<sub>x</sub> emissions for fixed sources. In recent years, it adopted the idea of trading emissions quotas, so that tighter regulations will not harm economic growth.

Each facility is assigned a yearly NO<sub>x</sub> emissions quota, and NO<sub>x</sub> emissions quota trading enables a company to sell/purchase and save the difference between the assigned value and the actual amount of emissions. This scheme achieves a net NO<sub>x</sub> reduction by gradually reducing the quota for each company<sup>[12]</sup>. This scheme provides an incentive for a company to introduce new NO<sub>x</sub> reduction technology because successful reduction enables the company to sell their excess quota to another company, compensating for the expense incurred in purchasing the new equipment. However, this scheme can have an adverse affect on economic growth if it is not accompanied by careful execution. For example,

Figure 2 : History of environmental regulations in the U.S.A and Europe



Source: Reference<sup>[11]</sup>

Table 2 : Regulation on NO<sub>x</sub> emission from fixed sources

Period	Regulation	Summary
1970-	Clean Air Act (CAA)	U.S. federal legislation enacted in 1970
1995-	Acid Rain Program	Aimed at SO <sub>2</sub> and NO <sub>x</sub> reduction and acid rain suppression via economically feasible means, including SO <sub>2</sub> emission quota trading. Encourages introducing energy efficiency that leads to environmental protection.
1999-	Ozone Transport Commission (OTC) NO <sub>x</sub> Budget Program	Targeted at some 900 thermal-power generation units and some 100 steam boilers in 12 eastern states. The upper limits of total emissions during the Ozone-season (May-Sept.) are regulated based on 1990 values. Max. values are assigned to each facility, allowing emission quota trading. Unused quota is marketable and can be carried over.
2004-	NO <sub>x</sub> State Implementation Plan (SIP) Call	Based on the above OTC NO <sub>x</sub> Budget Program, NO <sub>x</sub> emission quota trading is expanded to 22 eastern states and Washington DC.
2005-	Clean Air Interstate Rule (CAIR)	Aimed at substantial reduction of SO <sub>2</sub> and NO <sub>x</sub> emission from coal-fired power plants in 28 eastern states and Washington DC within ten years.
Under review	Clear Skies Act	Assign upper limits to SO <sub>2</sub> , NO <sub>x</sub> and mercury emissions from power plants. This legislation is binding and aims at a drastic reduction in emissions (70% reduction of the emission level in 2000)

**Table 3** : Emission limitations of new and existing fixed sources

Target material	Source	Limitation name	Target area	Summary
Criteria pollutants (Nox, SO <sub>2</sub> , CO, ozone, lead, PM)	New	BACT (Best Available Control Technology)	Attainment areas for federal ambient air quality standards of all six criteria pollutants	Facilities that emit >100 tons/year (specified category) or >250 tons/year of one or more of six criteria pollutants (NOx, SO <sub>2</sub> , CO, VOC, lead, PM) (large-scale source). As stringent as NSPS for the same type of new source.
		LAER (Lowest Achievable Emission Rate)	Non-attainment areas for at least one of the criteria pollutants	Facilities that emit >100 tons/year of five pollutants (NOx, SO <sub>2</sub> , CO, VOC, PM) (new source). Most stringent regulation level.
			Non-attainment areas for ozone and PM10	
		NSPS (New Source Performance Standards)	Attainment areas for federal ambient air quality standards of all six criteria pollutants	Targeted facilities include steel plants, lead/zinc refineries and rubber/tire factories, e.g. new sources of the selected category. A more stringent level is assigned to newly constructed facilities than the existing ones irrespective of their scale.
			Non-attainment areas for at least one of the criteria pollutants	
	Non-attainment areas for ozone and PM10			
Existing	RACT (Reasonably Available Control Technology)	Existing sources (Non-attainment areas for ozone and PM10)	Facilities that emit more than the specified amount of VOC yearly. Emission limit depends on the extent of ozone pollution (worst-case emission limit will be 10 tons/year or more).	

(Note) These Limitations are derived from CAAA (Clean Air Act Amendments, 1990)

Source: Reference<sup>[14]</sup>

in California, where emissions quota trading has been implemented since 1993, emissions went beyond the allocated quota triggering a sharp rise in the market rate for excess quota, finally bringing about power plant shutdowns in 2000<sup>[13]</sup>. This scheme can also lead to localized deterioration of atmospheric conditions because a facility is allowed to discharge a disproportionate amount of emissions by purchasing quota.

For new construction or large-scale modifications of a facility, the entity is required to install appropriate equipment to satisfy the regulation level for emissions according to the scheme shown in Table 3<sup>[14]</sup>. For example, for a newly constructed facility in regions where air pollution standards are satisfied, BACT (Best Available Control Technology) calls for the installation of equipment that is capable of removing all criteria pollutants. The equipment must be reasonably priced and be able to be run at a reasonable cost. LAER (Lowest Achievable Emission Rate) is the reference regulation applied to newly purchased equipment in regions where air pollution standards are not satisfied. For example, a newly installed gas turbine generator is required to produce emissions levels that are equal or lower than the minimum emissions

output of the existing generator. However when, for example, a coal fired power plant replaces boilers or other equipment, the plant would not have to install pollution control equipment to meet current standards if the cost of the pollution control equipment is less than 20 percent of the entire cost. This raises some doubt as to the actual effectiveness of the regulation<sup>[15]</sup>.

The Environmental Protection Agency (EPA) also performs an environmental technology verification program, including evaluation and verification of new environmental purification technologies developed in the private sector, the results of which are made public<sup>[16, 17]</sup>.

### 3 Catalyst technology for reduction of NOx emissions

Development of novel catalyst systems to eliminate NOx from gasoline-powered vehicle emissions is being actively undertaken. The three-way catalyst has been the industry standard for this purpose, but it is unsuitable for use in the newly developed lean-burn engines and diesel engines. Despite the success of selective catalytic reduction with ammonia (NH<sub>3</sub>-SCR) for fixed emission sources, the recent development

**Table 4 : List of NOx reduction catalysts**

For mobile source			For fixed source		
Type	Feature	Schematics	Type	Feature	Schematics
Three-way	<ul style="list-style-type: none"> <li>Gasoline-fueled vehicles</li> <li>Reaction at near equivalence point</li> <li>Typical composition: Pt-Pd-Rh-Al<sub>2</sub>O<sub>3</sub></li> </ul>		Catalytic combustion	<ul style="list-style-type: none"> <li>Natural gas fueled gas turbine combustor</li> <li>Low NOx emission combustion</li> <li>Typical composition: PdO-Al<sub>2</sub>O<sub>3</sub></li> </ul>	
NSR (NOx Storage and Reduction)	<ul style="list-style-type: none"> <li>Gasoline and diesel-fueled vehicles</li> <li>Can react in lean-burn conditions</li> <li>Typical composition: Pt-Ba-Al<sub>2</sub>O<sub>3</sub></li> </ul>		NSR (NOx Storage and Reduction)	<ul style="list-style-type: none"> <li>Natural gas fueled gas turbine</li> <li>Ammonia not required</li> <li>Typical composition: Oxidation catalyst-CaCO<sub>3</sub></li> </ul>	
SCR (Selective Catalytic Reduction)	<p>Urea-SCR:</p> <ul style="list-style-type: none"> <li>Large diesel-fueled vehicles</li> <li>Can react in lean-burn conditions</li> <li>Typical composition: V<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub></li> </ul> <p>HC-SCR:</p> <ul style="list-style-type: none"> <li>Gasoline fueled vehicles</li> <li>Typical composition: Ir-BaSO<sub>4</sub></li> </ul>		SCR (Selective Catalytic Reduction)	<p>NH<sub>3</sub>-SCR:</p> <ul style="list-style-type: none"> <li>Boiler/gas turbine using various fuels</li> <li>Typical composition: V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub></li> </ul>	

Source: Prepared from Reference<sup>[18-21]</sup>

of improved low NOx technologies may result in even more effective systems. Table 4 summarizes the mainstream catalyst technologies for NOx reduction<sup>[18-21]</sup>.

### 3-1 Catalyst for mobile sources (automobiles)

The “three-way” catalyst derives its name from the fact that the catalyst is capable of simultaneously removing CO, hydrocarbons (HC) and NO from automobile emissions. Researchers from Ford Motor Company discovered this phenomena in 1971, and TOYOTA Motor Corporation was the first to develop an automobile equipped with this catalyst system (1977)<sup>[22]</sup>. The three-way catalyst consists of a honeycomb-shaped substrate made of a ceramic or alloy with its surface coated by a washcoat, typically an aluminium oxides (Al<sub>2</sub>O<sub>3</sub>)-based material, with a large specific surface area. Ultra-fine particles consisting of catalytically active components, such as platinum (Pt), palladium (Pd) and rhodium (Rh),

are dispersed on the washcoat surface. The three-way catalyst has the disadvantage that it is susceptible to sulfur (S) poisoning. Because catalyst systems used for emission reduction, including the three-way type, typically operate in a high temperature environment, prevention of their thermal degradation is a major challenge. One possible solution is the development of self-regenerative catalysts<sup>[23]</sup>. Lean-burn engine vehicles have become popular in recent years, owing to their high thermal efficiency and better mileage. The three-way catalyst is not suitable for use in lean-burn engines, and NSR (NOx Storage and Reduction) catalysts are generally used. TOYOTA put a gasoline-powered vehicle equipped with this type of catalyst system on the market in 1994<sup>[22]</sup>. A variation of this system with the catalyst dispersed on a porous ceramic filter surface has also been developed, and it is capable of simultaneously removing NOx and PM from diesel vehicle emissions<sup>[24]</sup>. Because this catalyst

system, as well as the three-way type, suffer from deterioration caused by heat and poisoning, the creation of systems resistant to these effects is one of the future challenges.

The SCR catalyst can also be used for lean-burn engines, and a report illustrating selective NO<sub>x</sub> removal in which a hydrocarbon acts as the reductant was published in 1990<sup>[25]</sup>. Another SCR system that is primarily aimed towards reducing diesel-powered auto emissions using urea as a reductant is under consideration<sup>[19]</sup>. The main issues to be addressed for these catalysts include the prevention of NO<sub>x</sub> generation/emissions from the oxidation catalyst system that is typically placed downstream of the emission gas treatment system, together with enhancement of the NO<sub>x</sub> removal efficiency while the vehicle is running under low load conditions. The large physical size of currently available systems also leaves considerable room for improvement. In November 2004, Nissan Diesel Motor became the first company to put a large-size truck equipped with a urea SCR system on the market<sup>[26]</sup>. Deployment of a urea water station network is also being undertaken in anticipation of future adoption of automobiles equipped with urea SCR systems.

As described above, Japan is a step ahead of other industrialized countries, including the United States and European nations, with regard to emission gas purification technologies. The JCAP (Japan Clean Air Program), an industry-academic-government joint project involving the automotive and petroleum industries, was started in 1997 and has already yielded practical results. An example of these achievements is the evaluation study on the effect of sulfur content in fuel on emission reducing catalysts. The findings of this study resulted in a sulfur content regulation for gasoline and diesel fuel that was enforced in 2005<sup>[27]</sup>.

### 3-2 Catalysts for fixed sources

Two Japanese companies (Chubu Electric Power Company and Ishikawajima-Harima Heavy Industries Company) were the first (1979) to put NH<sub>3</sub>-SCR technology into practice for large-scale oil burning boilers<sup>[28]</sup>. This method injects NH<sub>3</sub> into the emission gas stream to efficiently remove NO<sub>x</sub>. The catalyst used in this process contains

vanadium oxides (V<sub>2</sub>O<sub>5</sub>) as the active component, dispersed in a honeycomb-shaped substrate made of titanium oxides (TiO<sub>2</sub>).

Application of the NSR (NO<sub>x</sub> Storage and Reduction) catalyst was first successfully applied to reduce the emissions from natural gas / low sulfur oil gas turbines by the now defunct U.S. company, Goal Line Environmental Technologies, (currently EmeraChem) in 1996<sup>[20]</sup>. This technique does not use ammonia, eliminating problems related to the storage/management/leak prevention of ammonia. Future goals for this technique include extension of the catalyst's operating life and cost reduction.

The NO<sub>x</sub> reduction technologies described above, both for mobile and fixed sources, all operate downstream of the combustion process, i.e. NO<sub>x</sub> is removed from the post-burning gas stream. An alternative approach is catalytic combustion, which prevents NO<sub>x</sub> generation in the burning process. In contrast to the conventional burning process, where atmospheric nitrogen and oxygen react to produce NO<sub>x</sub> in the high temperature region of the burner flame, catalytic combustion does not require such a high temperature flame over 1,500°C, resulting in ultra-low NO<sub>x</sub> formation. Palladium oxide (PdO) is generally used as the active catalyst component for this process. Kawasaki Heavy Industries was the first company (2002) to construct a practical natural gas turbine system using catalytic combustor and installed it in the U.S.<sup>[30]</sup>. Catalytica (U.S.) and Tanaka Kikinzoku Kogyo (Japan) developed the catalyst system<sup>[29]</sup>. Future challenges for catalytic combustion include its application in high-temperature, large-scale gas turbines and the ability to use diesel fuel.

## 4 Challenges ahead: Development of catalysts that minimize environmental impact

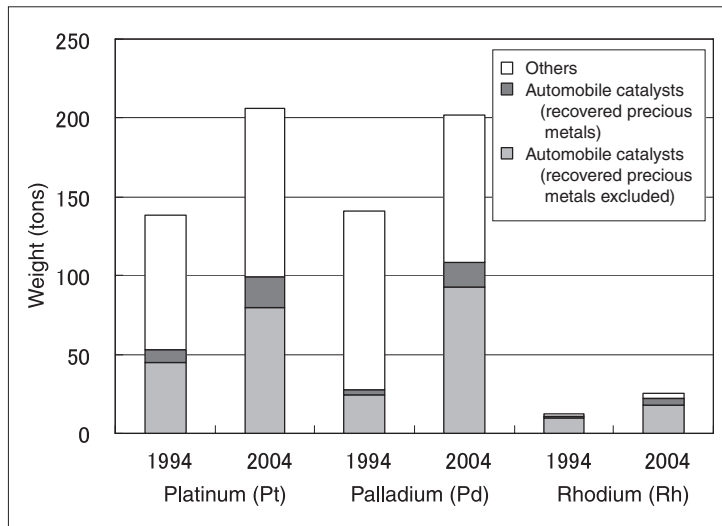
### 4-1 Usage of precious metals in catalysts

The catalysts used for automobiles generally have larger amounts of precious metals than those used in the chemical industry. Figure 3 shows the usage of Pt, Pd and Rh for catalysts<sup>[31]</sup>.

About 50% of Pt and Pd, and about 90% of Rh are consumed as the active components of automobile catalysts. It should also be noted that consumption of precious metals for automobile catalysts has significantly increased in the last ten years (approx. two-fold for Pt, and four-fold for Pd). Figure 4 shows the trend in precious metal usage (Pt+Pd) per automobile in Japan in relation to the progression of NOx emission regulations<sup>[31, 32]</sup>. Note that the figure is based on the purchased volume for automobile catalyst systems and includes inventory, so the actual consumption is somewhat below the figure shown. It is apparent that the strengthening of emission regulations is one of the main factors driving the increase in the volume of precious

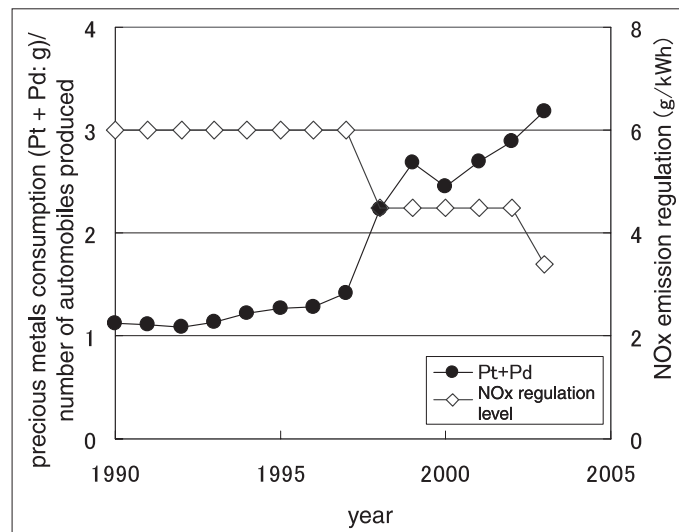
metal consumption for automobiles because ever larger quantities of precious metals are needed to enhance emission reducing capabilities. Another factor that has influenced the increase in precious metal consumption comes from their utility in solid polymer electrolyte fuel cells (the electrode catalyst uses precious metals). Fuel cells are being actively researched and developed for automobiles and distributed power generation. As already described, new environmental protection technologies aimed at fixed sources are also likely to use precious metals. Precious metals are a scarce resource, and about 90% come from only a handful of countries including Russia and South Africa. This uneven distribution makes them susceptible to the political and geological

Figure 3 : Global precious metal usage (automobile catalysts and others)



Source: Prepared from Reference<sup>[31]</sup>

Figure 4 : Trends in precious metal usage for automobiles (g/vehicle) and regulation level for diesel-fueled vehicles in Japan



Source: Prepared from Reference<sup>[31, 32]</sup>

situations prevailing in the producing countries. To strike a balance between supply and demand for stable pricing, initiatives have been taken to promote the recycling of precious metals and automobile companies try to contract directly with the mining companies to ensure mining is carried out according to a well organized schedule. Ongoing efforts to develop catalysts that require lower quantities of precious metals are also important. Automobile fuel with low sulfur content can also contribute to reducing precious metal consumption, because it extends the operational life of the catalyst.

The promotion of precious metal recycling needs to be advanced more than ever. As a basic method for recovering precious metals from used catalysts has already been established, future endeavors will be focused on streamlining the efficiency of the recovery system. Factors that have hindered the effective recovery of automobile catalysts include: illegal disposal, scrapping that disables component recovery, and export of junked automobiles to foreign countries. In Japan, new legislation came into effect in 2005 regarding automobile recycling, namely, "Law for the Recycling of End-of-Life Vehicles (End-of-Life Vehicle Recycling Law)" to promote effective utilization of junked vehicles. This law ordains that vehicle disposal-related costs must be pre-paid when the user purchases a new vehicle, eliminating the need to impose an extra charge when the vehicle goes out of commission. This scheme is expected to enhance precious metal recovery from junked automobiles. However, since automobiles purchased before this law was enacted will still require a disposal charge, it is feared that a temporary decrease of recovery may occur because of the ensuing charge<sup>[33]</sup>.

#### 4-2 *Environmental catalyst technologies capable of addressing energy/environmental concerns*

To address energy conservation and the global warming problem, Japanese Diet enacted the "Law concerning the Rational Use of Energy (Energy Conservation Law)" in 1998 and revised it aiming at improving fuel efficiency<sup>[34]</sup>. However, reduction of carbon dioxide (CO<sub>2</sub>) emissions

from automobiles can be achieved through other measures, including: mixing of bio-ethanol into gasoline, mixing of bio-diesel and diesel fuel, and utilization of natural gas and diesel oil as automobile fuel.

The refining process from crude to diesel oil requires less energy than the conversion process into gasoline; CO<sub>2</sub> emissions associated with the refining 1 kg of diesel oil are less than half that of refining 1 kg of gasoline<sup>[35]</sup>. Provisional estimates indicate that the CO<sub>2</sub> emissions from a diesel-powered automobile are approximately 10% lower than those from a gasoline-powered vehicle<sup>[36]</sup>. Further reduction is expected by hybridizing a diesel engine with an electric motor. On the other hand, diesel-powered vehicles generally produce more PM and NO<sub>x</sub> than gasoline vehicles<sup>[7]</sup>.

An alternative option, the utilization of CNG (Compressed Natural Gas) powered automobiles, has been underway for some time. This type of vehicle is more suited for short-distance trips because its range is generally less than gasoline/diesel powered vehicles. CO<sub>2</sub> emissions from CNG vehicles are estimated to be equal to or slightly higher than diesel oil vehicles. The CNG vehicle requires a lean-burn engine to improve thermal efficiency, and development of a catalyst system to reduce emissions from this type of engine remains a challenge. Utilization of biomass fuel is an alternative solution, but research into the effect of biomass fuel emissions on the environment is still at an early stage and requires further study<sup>[7]</sup>.

#### 4-3 *Problems associated with the dissemination of co-generation systems*

Figure 5 shows the installation history of co-generation systems in Japan<sup>[37]</sup>. Introduction of co-generation systems is actively promoted in Japan, especially in urban areas, for purposes such as saving energy, minimizing CO<sub>2</sub> emissions, and as a back-up power source in emergency situations. Co-generation installations with a capacity less than 112.5 MW are excluded from environment assessment targets, and the NO<sub>x</sub> emission regulation in Tokyo and others is more lenient for small engines and turbines, as shown in Table 5<sup>[38]</sup>. Regulation of total NO<sub>x</sub> emissions

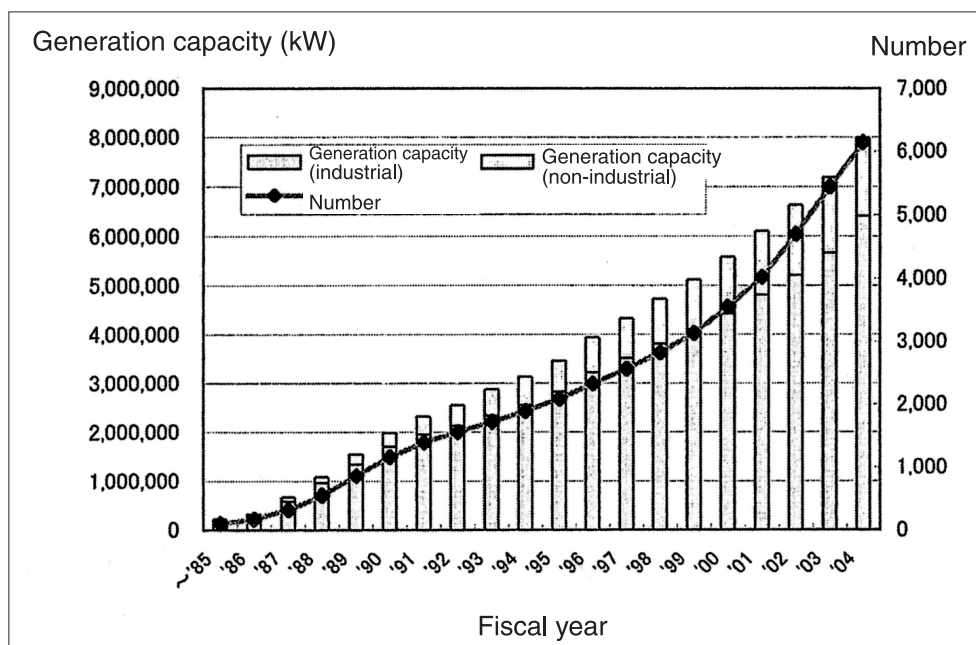


is also lenient for installations that consume small amounts of fuel. As a result, small co-generation installations discharge higher concentrations of NOx than the larger ones. According to a report<sup>[39]</sup>, co-generation installations in the Tokyo metropolitan area emit 0.81 g/kWh of NOx on average, which is roughly eight times larger than the overall average of power plants in total NOx regulated areas, and four times larger than the fossil fuel power plants average. The number of co-generation installations is expected to rise continuously, and the need for tighter NOx regulation of these installations in the future would be inevitable. Installation of NH<sub>3</sub>-SCR systems in smaller power generation plants,

such as co-generation facilities, has a number of disadvantages. For example, it requires extra space and equipment for storage and management of ammonia (toxic) gas, as well as equipment for gas leak monitoring. Development of optimum NOx removal technology for these small installations demands urgent attention.

Overall environmental pollution in Japan has been considerably reduced due to rigorous regulations, together with environmental technologies that have undergone significant advances. In terms of environmental measures for large facilities, such as factories and power plants, as well as gasoline-powered automobiles, Japan is a world leader. The strengthening of

Figure 5 : Trends in accumulative co-generation system installations in Japan



Source: Reference<sup>[37]</sup>

Table 5 : Selected values from governmental/municipal NOx regulation standards (gas turbine)

Unit : ppm (O<sub>2</sub>=16%)

As of 2005

Scale		Guideline of Tokyo		Air pollution control law
		1st category area	2nd category area	Entire country
Gas fuel combustion	>= 50,000 kW	10	10	70
	>= 2,000 kW	25	35	
	< 2,000 kW	35	50	
Liquid fuel combustion	>= 50,000 kW	10	10	
	>= 2,000 kW	25	50	
	< 2,000 kW	35	60	

(Note) Target : facilities that consume more than 50 l/h crude equivalent of fuel.

1st category area : 23 metropolitan wards, Musashino-City, Chofu-City, (defunct) Hoya-City, Komae-City.

2nd category area : all other areas excluding those above

Source: Prepared from reference data

environmental regulations is the most direct and effective measure to improve environmental health. However, it should also be noted that environmental regulation could also harm the development and dissemination of new technology. Outstanding technology that can easily surpass the regulation value may not be adopted if it is too expensive (e.g. due to high development costs) compared with an average technology that is just able to meet the criteria, or because it lacks a proven track record. For example, if the NO<sub>x</sub> regulation standard is set to 10 ppm, the majority tends to prefer the technology which can solve 10 ppm problem over a more advanced the other technology which can solve 5 ppm issue if the latter is more costly.

In the U.S., the EPA and state authorities have introduced various incentives, including environmental technology verification programs and NO<sub>x</sub> emissions quota trading, to promote development and dissemination of new NO<sub>x</sub> removal technologies. Facilities that are required to meet the BACT and LAER regulation targets have to introduce more sophisticated environmental technologies. These measures appear to have been effective in promoting new NO<sub>x</sub> reduction technologies, as well as in providing economic incentives. Japan has also introduced various measures to support development of new environmental technologies: the pilot project of the environmental technology verification <sup>[40]</sup>, introduction of the BACT approach to environmental impact assessment<sup>[Note 1][41]</sup>, and the promotion project to disseminate NO<sub>x</sub> emission guideline compliant equipment (for small equipment, such as hot water apparatus, that fall outside the emission regulation) <sup>[8]</sup>. However, the pilot project of the environmental technology verification that started in 2003 targeted selected areas of technology. The environmental impact assessment covers only large-scale facilities and excludes small installations. The NO<sub>x</sub> emission guideline compliant equipment does not cover all small equipment. For example, small generators for emergency use are excluded from the guideline.

## 5

## Proposals for environmental catalyst development: Towards a better environment

Based on the agenda described in the previous chapters, we present the following proposals for the enhancement of environmental catalyst technology in Japan.

### (1) Promotion of technology for reducing the use of precious metals

Research aimed at reducing precious metal usage in catalysts has a long history. Because of the complex nature of catalytic reactions (involving atomic and molecular level phenomena), analysis has been largely performed on a trial-and-error basis requiring an extensive range of experiments to cover all combinations. Recent advancement of analytical methods has gradually changed this situation. Details of the mechanisms of catalytic reaction and catalyst degradation have been elucidated, and computer simulations have reached the stage that they have become helpful in further deepening our understanding. A good example of these advancements is the study of self-regenerative catalysts. The growth suppression mechanism of ultra-fine particles of Pd was elucidated by means of synchrotron radiation X-ray analysis equipment installed in Japan (Japan Synchrotron Radiation Research Institute (SPring-8)). According to this mechanism, Pd usage can be reduced by 70-90% <sup>[23]</sup>. The same approach is expected to also apply to other precious metals and will contribute to the reduction of their usage in catalysts <sup>[42]</sup>. Computer simulations are being actively used to understand the reaction mechanism at a molecular level. Typical examples include the search for active catalysts <sup>[43]</sup> and elucidation of the sintering processes in catalytic reactions using μm-level simulations <sup>[44]</sup>. The use of state-of-the-art analytical instruments and simulations shows great promise in enabling much more efficient catalyst development, ultimately resulting in the substantial reduction of precious metal usage. These novel methodologies will help elucidate hitherto unknown mechanisms, paving the

way for technical breakthroughs. Large-scale equipment that exceeds the financial resources of companies or universities should be introduced using the national budget. Although highly sophisticated analytical instruments, such as SPring-8, present difficulty in terms of both operation and data analysis, close cooperation between universities/research institutes (with advanced information regarding the measurement techniques) and companies developing catalysts, will enable streamlining of the development process. Research into non-precious metal containing catalysts for use in automobiles is an important issue. Practical application, however, has not yet been realized. Universities and national research institutes should spearhead basic research in this area.

## **(2) Enhancement of precious metal recycling**

Compliance with the End-of-Life Vehicle Recycling Law and prevention of the unlawful disposal of junked vehicles are needed to increase the recovery yield of used catalysts. In view of the fact that an enormous number of new/used vehicles are exported overseas, the development of recycling systems in the destination countries, especially in developing countries, should be an effective way of attaining a higher recovery yield of used catalysts. In this respect, governmental support projects, such as the Green Aid Plan<sup>[Note2][45]</sup>, will provide incentives for developing countries to start constructing recycling systems for junked vehicles and used precious metals.

## **(3) Development of environmental catalyst technology that directly contributes to solving the energy problem**

Addressing the energy problem, especially CO<sub>2</sub> reduction, is an urgent issue. A typical challenge is the reduction of emissions from diesel-powered automobiles to the level of gasoline-powered vehicles. The dissemination of the automobiles with ultra-clean exhaust emissions will greatly contribute to the reduction of crude oil consumption and CO<sub>2</sub> emissions. In view of the projected broader utilization of bio-mass and natural gas in the near future, which will also contribute to CO<sub>2</sub> reduction, evaluation of the

nature of exhaust gas from bio-mass fuel and the development of an exhaust cleaning catalyst suitable for use with CNG and bio-mass fuels will be important. For better emission reduction performance, engines and catalyst systems should be fully integrated, which necessitates the coordinated development of engine and catalyst. Following this approach, a novel hybrid emission reduction system that incorporates plasma technology and catalysis is under consideration. Use of plasma may make it possible to activate a catalyst at lower temperatures. Previously, activity was only attained at elevated temperatures<sup>[46,47]</sup>. The combination of a photo-catalyst and plasma technology for air purification system was pioneered in Japan and has already been utilized in commercial applications. Continued refinement of this hybrid system may mean that the energy required for emission reduction can be reduced.

## **(4) Promotion of technological competition that contributes to the advancement of environmental technology**

For Japan to maintain its leading position in the environmental catalyst arena, the promotion of competition is necessary so that developers of superior technologies are financially rewarded. Possible measures for this purpose include expansion of the areas targeted by the pilot project of the environmental technology verification, and also expanding the range of equipment included in the low NO<sub>x</sub> equipment promotion project. In the U.S., a variety of regulations have been implemented to help dissemination of sophisticated environmental technologies. It would be useful to introduce these measures to small equipments excluded from application of the environmental impact assessment in Japan in a fashion suitable to our country. NO<sub>x</sub> emissions quota trading will be a powerful incentive for the development of low NO<sub>x</sub> emission technology. However, as the large-scale blackout that occurred in California clearly illustrates, suitable modification of this approach is needed in order for Japan to adopt it.

## **Acknowledgements**

The authors wish to express their gratitude

to the many people that helped prepare this report. Among them, special thanks are extended to the following researchers: Mr. Akihiko Abe and Mr. Hisashi Furukawa (Tanaka Kikinzoku Kogyo K.K.) for useful discussion on catalytic combustion technology. Dr. Shinichi Kajita (Kawasaki Heavy Industries, Ltd), Mr. Kotaro Morita and Mr. Katsuyasu Yamasaki (ALSTOM K.K.) for information on low NO<sub>x</sub> emission technologies implemented in the U.S., and last, but not least, Dr. Tohru Yamamoto (Central Research Institute of Electric Power Industry) for information on SPring-8.

### Notes

- [Note 1] When assessing the effects on the environment, criteria are added to evaluate if the business entity has adopted the optimal technology available to reduce the environmental impact.
- [Note 2] Governmental projects that assist developing countries to start energy and environmental protection measures, in which Japanese environmental protection technology is actively used.

### References

- [1] Kenichi Tanaka, Kenji Tamaru, "Science of catalysis", Sangyo Tosho, p.3-13, July 1988. (in Japanese)
- [2] Hirokazu Fukushima, "Air Pollution Monitoring in East Asia", Science & Technology Trends —Quarterly Review—, No.18, January 2006: <http://www.nistep.go.jp/achiev/ftx/eng/stfc/stt018e/qr18pdf/STTr18.pdf> (as of January 31, 2006)
- [3] Written material: "Road Pocketbook", Japan Highway Users Conference, 1999. (in Japanese)
- [4] Yoshiaki Shibata, "A Trend of Exhaust Emission Regulation and Ambient Air Quality in Japan through JCAP Activities", IATSS Review, Vol. 29, No.2, p.95-102 (October 2004). (in Japanese)
- [5] "Guideline for Automobile NO<sub>x</sub>/PM Reduction Law", Ministry of the Environment —Ministry of Land, Infrastructure and Transport, August 2002: <http://www.env.go.jp/air/car/pamph2/all.pdf> (as of October 16, 2005). (in Japanese)
- [6] "Working Towards a Sound Automotive Future", Japan Automobile Manufacturers Association, Inc.: [http://www.jama-english.jp/publications/working\\_towards.pdf](http://www.jama-english.jp/publications/working_towards.pdf) (as of October 16, 2005)
- [7] "Future Policy for Motor Vehicle Exhaust Emission Reduction (8th report)", Central Environment Council, April 2005: [http://www.env.go.jp/council/toshin/t07-h1702/t07-h1702\\_1.pdf](http://www.env.go.jp/council/toshin/t07-h1702/t07-h1702_1.pdf) (as of October 2005). (in Japanese)
- [8] "Quality of the Environment (White Paper)", Ministry of the Environment: <http://www.env.go.jp/en/w-paper/> (as of October 16, 2005)
- [9] "Report on fuel for the next generation low pollution automobiles and related technical trends", Automobile Division, Manufacturing Industries Bureau, August 2003 : <http://www.meti.go.jp/kohosys/press/0004362/1/030808teikougaisya.htm> (as of October 16, 2005). (in Japanese)
- [10] "Report on the state of air pollution in FY 2004", Ministry of the Environment: <http://www.env.go.jp/air/osen/> (as of October 16, 2005). (in Japanese)
- [11] Shigeru Nakamura, "Paint Technologies for Environmental Protection —Automotive Coatings—", Toryo no Kenkyu (Research on Coatings), No.137, p.24-30, October 2001. (in Japanese)
- [12] Mikio Takai, Yoshiki Iinuma, Hiroshi Inoue, Tomohiro Hujii, "Emissions quota trading in the U.S. and European Union", Kaigai Denryoku, p.10-24, August 2003. (in Japanese)
- [13] "Current status of refurbishment of power generation in foreign countries and its regulatory challenges", Agency for Natural Resources and Energy, Ministry of Economy, Trade and Industry, April 2001: <http://www.meti.go.jp/kohosys/press/0001505/> (as of October 16, 2005). (in Japanese)
- [14] "Survey report on evaluation method using a best available technology, FY1998", Ministry of the Environment, March 1999: <http://assess.eic.or.jp/houkokusho/bat9903/> (as of October 16, 2005). (in Japanese)
- [15] Kuniko Urashima, "The Current Argument between Scientists and Government for Science and Technology Policy in U.S.",

- Science & Technology Trends —Quarterly Review—, No.15, April 2005:  
<http://www.nistep.go.jp/achiev/ftx/eng/stfc/stt015e/STTqr15.pdf> (as of October 16, 2005)
- [16] “Environmental Technology Verification Program”, U.S. Environmental Protection Agency: <http://www.epa.gov/etv/> (as of October 16, 2005)
- [17] “EPA’s Environmental Technology Verification Program”, International Symposium on Environmental Technology Verification, Tokyo, Japan, February 2003:  
[http://etv-j.eic.or.jp/pdf/ab/01/us\\_e.pdf](http://etv-j.eic.or.jp/pdf/ab/01/us_e.pdf) (as of October 16, 2005)
- [18] Naoto Miyoshi, Tsuneyuki Tanizawa, Shin-ichi Takeshima, Naoki Takahashi, Kouichi Kasahara, “Development of NOx Strage-Reduction 3-Way Catalyst for Lean-Burn Engines”, Toyota Technical Review, Vol.44, No.2, p.24-29, 1994.(in Japanese)
- [19] “Report on the establishment of a committee for urea SCR system technology”, Ministry of Land, Infrastructure and Transport: [http://www.mlit.go.jp/kisha/kisha03/09/091218\\_.html](http://www.mlit.go.jp/kisha/kisha03/09/091218_.html) (as of October 16, 2005). (in Japanese)
- [20] L. Czarnecki, R. Oegema, J. fuhr, R. Hilton, “SCONox™-Ammonia Free NOx Removal Technology for Gas Turbines”, Proceedings of 2000 International Joint Power Generation Conference, Miami Beach, Florida, IJPGC2000-15032, July 2000.
- [21] Yasushi Ozawa, “Development Trend of Catlytic Combustor”, Journal of the Combustion Society of Japan, Vol.47, p.40-47, 2005. (in Japanese)
- [22] “Handbook of Environmental Catlyst”, ed. Masakazu Iwamoto, NTS, p.268-274, November 2001. (in Japanese)
- [23] “Drastic reduction of precious metal usage by means of self-regenerative emission reduction catalysis for automobiles”, Science & Technology Trends, July 2003.:  
[http://www.nistep.go.jp/achiev/ftx/jpn/stfc/stt028j/0307\\_02\\_topics/200307\\_topics.html](http://www.nistep.go.jp/achiev/ftx/jpn/stfc/stt028j/0307_02_topics/200307_topics.html) (as of October 16, 2005). (in Japanese)
- [24] “TOYOTA’s new catalyst removes PM and NOx simultaneously”, Car & Maintenance, Vol.54, No.10, p.33-35, 2000. (in Japanese)
- [25] Masakazu Iwamoto, Hidenori Yahiro, Yoshihiro Yu-u, Seiji Shundo, Noritaka Mizuno, “Selective Reduction of NO by Lower Hydrocarbons in the Presence of O<sub>2</sub> and SO<sub>2</sub> over Copper Ion-exchanged Zeolites”, Shokubai (Catalyst), Vol.32, No.6, p.430-433, 1990. (in Japanese)
- [26] “Nissan Diesel Commercializes FLENDs Technology for Compliance with Japan’s New Long-term diesel emissions regulation”, Nissan Diesel: <http://www.nissandiesel.co.jp/e/newsrelease/2004/1007.html> (as of October 16, 2005)
- [27] Tatsuo Omata, “Outline of JCAP I Activities and the Outcome”, Journal of Japan Institute of Energy, Vol.82, No.5, p.242-245, 2003, (in Japanese)
- [28] “Handbook of Environmental Catlyst”, ed. Masakazu Iwamoto, NTS, p.518-524, November 2001. (in Japanese)
- [29] R. A. Dalla Betta, N. Ezawa, K. Tsurumi, J. C. Schlatter, S. G. Nickolas, U.S. Patent, No.5183401, February 1993.
- [30] “OEM Relationships”, Catalytica Energy Systems: <http://www.catalyticaenergy.com/xonon/oem.html> (as of October 16, 2005)
- [31] “Platinum 1999”, Johnson Matthey (May 1999), “Platinum 2005”, Johnson Matthey (May 2005)
- [32] “Handbook of land transportation”, “Statistics on automobile transportation”, Ministry of Land, Infrastructure and Transport: <http://toukei.mlit.go.jp/saisintoukei.html> (as of October 16, 2005). (in Japanese)
- [33] “Summary minutes of the (9th) joint meeting between the Automobile Recycling Working Group, the Waste and Recycling Subcommittee, the Environmental Panel, the Industrial Structure Council, and the Automobile Recycling Expert Committee”, the Waste and Recycling Panel of the Central Environment Council, July 2005 : <http://www.env.go.jp/council/03haiki/y035-09a.html> (as of October 16, 2005). (in Japanese)
- [34] “Law concerning the Rational Use of Energy”, The Energy Conservation Center, Japan: [http://www.eccj.or.jp/law/rational\\_use\\_of\\_energy.html](http://www.eccj.or.jp/law/rational_use_of_energy.html) (as of October 16, 2005)
- [35] “Survey report on the life-cycle inventory of transport fuel —a comparison of fuel cell cars and conventional cars”, Japan Petroleum

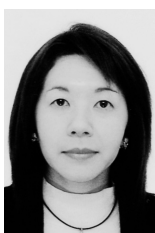
- Energy Center, PEC-2001L-04, March 2002. (in Japanese)
- [36] "Report on dissemination and future prospective of clean diesel-powered automobiles", Automobile Division, Manufacturing Industries Bureau, 2005 : <http://www.meti.go.jp/report/data/g50418bj.html> (as of October 16, 2005). (in Japanese)
- [37] "5. Trends in thermal energy systems", Journal of Japan Institute of Energy, Vol.84, No.8, p.685-689, 2005. (in Japanese)
- [38] "General manual for co-generation", Japan Cogeneration Center, Tsusanshiryochosakai, p.556-565, June 2000. (in Japanese)
- [39] Ayumu Sato, Yoichi Ichikawa, "Estimation of Annual Emissions of NO<sub>x</sub> Discharged from Cogeneration Systems in the Tokyo Metropolitan Area", Report T03009: Central Research Institute of Electric Power Industry, February 2004. (in Japanese)
- [40] "The Pilot Project of The Environmental Tehnology Verification of Japan": <http://etv.jec.or.jp/en/index.html> (as of October 16, 2005)
- [41] "Guideline on the evaluation method based on the utilization of best available technology", Ministry of the Environment, August 2000: <http://assess.eic.or.jp/houkoukusho/bat0003/index.html> (as of October 16, 2005). (in Japanese)
- [42] Hirohisa Tanaka, "Perovskite catalyst with self-regenerative function for precious metal nano-particles", Proceeding of 96th Catalysis Society of Japan Meeting A, p.198, September 2005. (in Japanese)
- [43] Kei Kuramoto, Shuichi Kubo, "Catalyst design based on theoretical considerations of surface catalytic reactions of exhaust cleaning catalysts", Proceeding of 96th Catalysis Society of Japan Meeting A, p.220, September 2005. (in Japanese)
- [44] Momoji Kubo, Ryouta Ishimoto, Jung Changho, Hideyuki Tsuboi, Michihisa Koyama, "Elucidation of catalytic sintering processes using  $\mu$ m-scale simulations", Proceeding of 96th Catalysis Society of Japan Meeting A, p.234, September 2005. (in Japanese)
- [45] "5. Green Aid Plan (International Cooperation for Energy and the Environment)": <http://www.meti.go.jp/english/information/downloadfiles/cODA205e.pdf> (as of October 16, 2005)
- [46] K. Urashima, J.-S. Chang, J. Y. Park, D.C. Lee, A. Chakrabarti and T. Ito, "Reduction of NO<sub>x</sub> from Natural Gas Combustion Flue Gas by Corona Discharge Radical Injection Techniques", Trans. IEEE Ind. Appl. Soc., vol. 34, No.5, p.934-939, 1999.
- [47] K. Urashima and J.-S. Chang, "Removal of Volatile Organic Compounds From Air Streams and Industrial Flue Gases by Non-Thermal Plasma Technology", Trans. IEEE DEIS. Soc., vol.7, No.5, p.602-614, 2000.



**Yasushi OZAWA, Ph.D.**

Affiliated Fellow, NISTEP  
Energy Engineering Research Laboratory, Central Research Institute of Electric Power Industry  
<http://criepi.denken.or.jp/en/>

Doctor of Engineering. After being engaged in catalytic combustion research for a number of years, Dr. Ozawa's current focus is on a clean-up catalyst for gasification power generation and combustion technology of liquid fuels.



**Kuniko URASHIMA, Ph.D.**

Head of Environment and Energy Research Unit, Science and Technology Foresight Center

Doctor of Engineering. Before Dr. Urashima assumed her present position, she was engaged in various research relating to the detoxification of environmentally hazardous materials (exhaust gas, discharged water, waste materials, etc.) at industries and universities in Japan, Canada, US and France.