# Recent progress in environmental catalytic technology

Katsunori Yogo and Masamichi Ishikawa

*Interdisciplinary Department, Frontier Science Institute, Mitsubishi Research Institute, Inc., 2-3-6 Otemachi, Chiyoda-ku, Tokyo 100-8141, Japan*

Recent progress and trends in environmental catalytic technology in Japan are described with emphasis on the catalysts having hybridized functions. In addition to automobile exhaust cleaning, use of environmental catalysts such as titanium oxide photocatalysts is rapidly growing for the control of residential environments, e.g., antimicrobial activity and odor control, as life styles change gradually and the living environment is deteriorating considerably. Many new catalysts are evolving through hybridization of functions. The market of environmental catalyst products in 2005 is estimated 2,000 billion yen/year (photocatalyst: 1,100 billion yen/year).

**Keywords:** environmental catalyst, titanium dioxide, photocatalyst, hydrophobilicity, hybridized functions, automotive catalyst

## 1. Introduction

As the concern about global and regional environmental problems grows, environmental catalysts have become more and more important. The word “environmental catalysts” has gained wide acceptance, and significant progresses have been made with respect to both fundamental research and applications of environmental catalysts [1–5]. Since environmental catalysts must possess high activity, high selectivity and high durability under severe conditions, the following areas have been focused on developing novel classes of catalysts [6]:

(1) control of active sites at molecular and atomic levels,

(2) achievement of high activity and selectivity through functional hybridization,

(3) development of highly durable materials, and

(4) catalytic reaction engineering for extremely severe conditions.

Two recent breakthroughs in this field were Toyota’s exhaust-cleanup catalyst for automotive lean-burn engines and the utilization of the superhydrophilic properties of $TiO_2$ photocatalyst invented by TOTO Ltd., both representing significant progresses in the areas described above (figure 1). Toyota’s technology was achieved by the control of active sites on solid surfaces (integrated functions) and practical applicability; the combination of NO oxidizer, absorption of generated $NO_2$ on the substrate, and control of exhaust gas composition with the aid of a computer [7]. The superhydrophilic properties of $TiO_2$ photocatalyst is a serendipitous discovery through combining hydrophilicity and photocatalytic activity, providing novel functionality [8].

Thus the achievement of high-performance environmental catalysts through functional hybridization has been the major concept of catalyst design. The present article reviews recent progress in environmental catalysts with emphasis on functional hybridization.

## 2. Background of the growth in environmental catalyst technology

Use of environmental catalysts is rapidly growing for the control of residential environments, e.g., antimicrobial activity and odor control, as life styles and the living environment change rapidly. Pollution by $NO_x$ and diesel exhaust particles from buses and trucks as well as hazardous chemicals such as dioxin emitted from waste incineration have recently become major serious problems. Meanwhile, improvements in the Japanese life style have made houses more air-tight than ever. We are now liv-

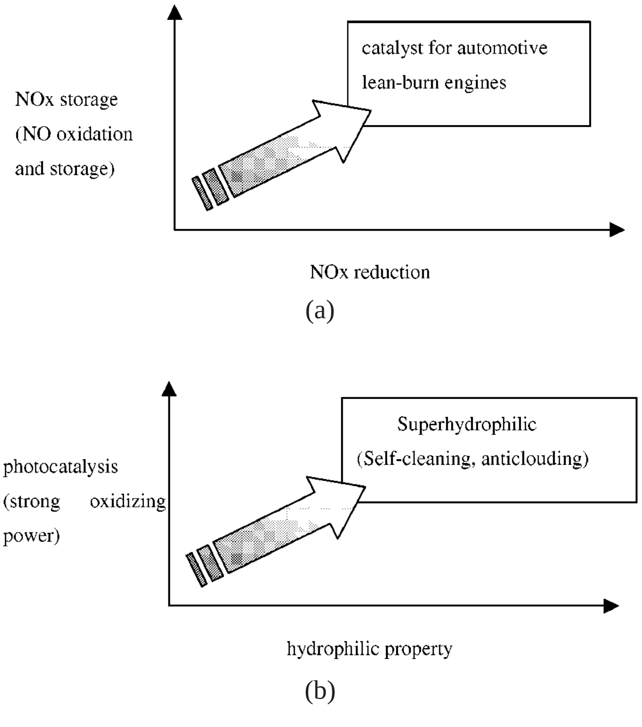


Figure 1. Typical examples of achievement of high performance through functional hybridzation. (a) $NO_x$ storage-reduction (NSR) catalyst: Toyota, (b) Hydrotect: TOTO.

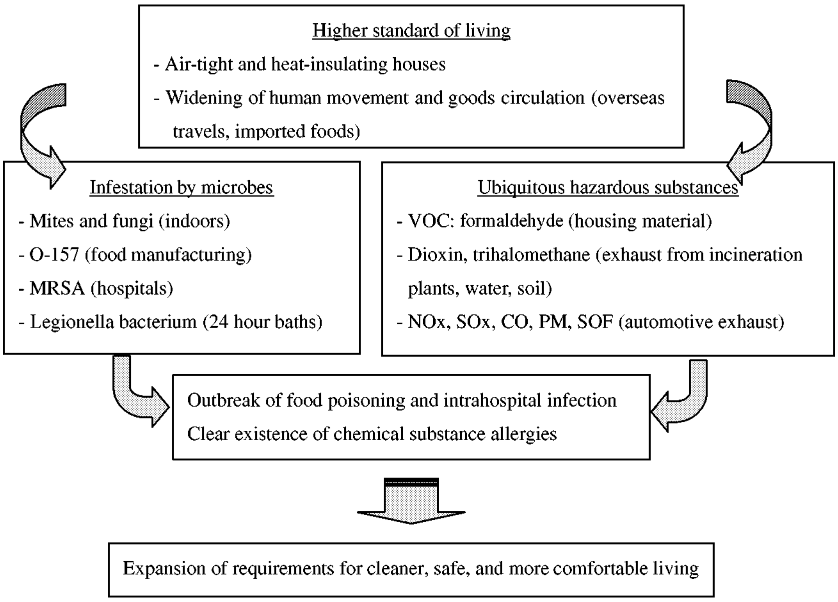


Figure 2. Background of wider uses of environmental catalysts in residences.

Table 1
Use of environmental catalysts in residences.

| Function | Catalysts | Object | Principal effects | Example of application |
|---|---|---|---|---|
| Oxidation of organic substances | Metals (complex) (Ag, Cu, Zn, phthalocyanine) | Gas phase (air cleaning) | Removal of odor and hazardous substances, sterilization | Air cleaner, air conditioner, deodorizing appliances (cooker, heater, refrigerator, vacuum cleaner), kitchen waste processor |
| | Oxides ($MnO_2$, zeolite) | Liquid phase (water cleaning) | Removal of odor and hazardous substances, sterilization | Water reservoir,<br>glassware,<br>water purifier,<br>sterilization of bathtub |
| | Noble metals (Pt, Pd, etc.)<br>Photocatalysts ($TiO_2$) | Surfaces (surface cleaning) | Antimicrobial activity (anti-polluting), self-cleaning | Tiles, sanitary porcelains, kitchen knives, cutting board, touch;<br>Sensor, antimicrobial fibers, lighting equipment, glass, blinds, inner walls of cooking chambers |
| | Noble metals (Pt, Pd, etc.) | Heat of reaction (exothermic) | Heating, warming; catalyzed combustion | Cordless irons, hair colors, warm clothes (jackets and belts), lighters |
| Super-hydrophilicity | Photocatalysts ($TiO_2$) | Surfaces (surface modification) | Anticlouding, anti-polluting, easy-cleaning | Tiles, mirrors |

ing in odor-enclosing and microbe-infested environments. Increases in overseas travel and food imports are also increasing risks of infection. Antimicrobial measures have attracted public attention since the recent panic over the colon bacillus O-157 (figure 2).

Thus improvement in the living environment has attracted public concern. Table 1 lists environmental catalysts for residential uses. They are divided into titanium oxide photocatalysts and combustion catalysts. Many of these use the reaction with oxygen to decompose organic compounds. Various products have been developed to remove air-borne odor substances and microbes. Their application is now expanding from indoor to outdoor. Examples are jackets, belts and cushions in which exothermic catalytic combustion reaction over platinum catalysts is utilized.

Table 2 collects examples of hybridization of catalytic functions. Photocatalysts are finding various new markets through enhanced functionality attained by the combination of photocatalysis and the functions of base materials. The key technique for the development of these products was cementing two different materials together. Details of these technologies are described below.

Table 2
Examples of functional hybridzation.

| Catalyst | Hybridized function | Application | Inventer |
|---|---|---|---|
| $TiO_2$ photocatalyst | Photocatalysis + super-hydrophilic property | Anti-polluting | TOTO Ltd. |
| | UV excitation + visible light excitation | Photocatalysis by visible light hydrophilic/hydrophobic switching | Osaka Pref. Univ.<br>TOTO Ltd. |
| | Adsorption (active carbon) + photocatalysis | Removal of trace components | Mitsubishi Chemical Co. |
| | Adsorption (apatite) + photocatalysis | Reactant selectivity | National Ind. Res. Inst. of Nagoya |
| | Photocatalysis + inert surface ($SiO_2$ coating) | Musk melon structure (binding with organic compounds) | Res. Inst. of Ind. Prodcts. Tech, Gifu |
| | Photocatalysis + surface fine structure | Super-hydrophobic property | Tokyo Univ. |
| | NO oxidation (photocatalysis) + adsorption | $NO_x$ removal (air) | National Insutitute for Resources & Environment |
| Oxidation catalyst (noble metal) | Adsorption (sepiolite) + decomposition | Deodorization | Matsushita Electric Co. |
| | Mobile + heating | Warm clothes (jackets and belts) | Matsushita Electric Co. |
| | Ultrafine particle + support interaction | Deodorization | Osaka National Research Inst. |
| Automotive exhaust catalyst | $NO_x$ adsorption (NO oxidation) + $NO_x$ reduction | Automotive lean-burn exhaust | Toyota Motor Co. |
| | HC adsorption + NO reduction | Cold start exhaust clean-up (HCs) | Nissan Motor Co. |
| | Three-way catalyst + electric current | Cold start exhaust clean-up (HCs) | Nissan Motor Co. |

## 3. Antimicrobial and anti-polluting applications

Photocatalysts are superior to conventional silver-based antimicrobial agents in such that they have stronger oxidizing power, higher stability and a longer service life. Recently, a technique was developed to coat various surfaces with these photocatalysts while maintaining its antimicrobial activity. They, however, are used in combination with silver or copper agents, since the photocatalysts are not effective in dark places [9].

Photocatalysts for pollution prevention have attracted interest in relation to outdoor applications. One example is covers of lamps installed in highway tunnels. Other products include sound-insulating boards, guardrails, and tent canvases. One of the conventional anti-polluting measures is the use of water-repellant paint for outer walls of buildings. Photocatalysts can be added to this type of paint to maintain its water repelling ability by decomposing organic dirt. Such a product is already in the market.

On the other hand, the superhydrophilicity of $TiO_2$ photocatalyst has been utilized in the development of a novel anti-polluting product. The superhydrophilic photocatalyst was invented by TOTO Ltd. in 1996 (figure 3). The technology is based on the phenomenon that the photo-activated titanium oxide has nearly zero contact angles against water. It has been applied in anti-polluting processing of glasses [10,11], mirrors, and car bodies; all these are totally new application fields for photocatalysts [12–14]. This technology will find a much greater market when made applicable to organic materials such as fibers and plastics.

## 4. Deodorant and air-cleaning applications

Titanium oxide catalysts are not efficient enough for the removal of hazardous substances in large quantities; rather they are suitable for removing specific pollutants present in air or water in trace amounts. Many bad-smelling materials are perceived by humans at levels as low as ppb orders so

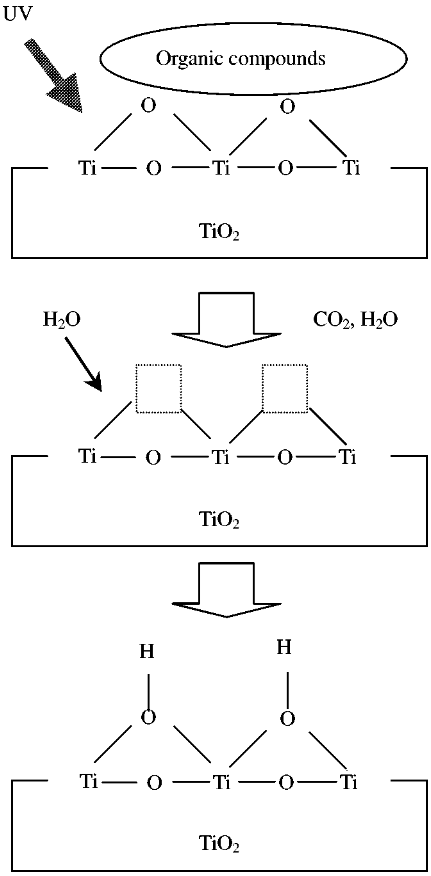


Figure 3. Mechanism of the superhydrophilic property of the $TiO_2$ photocatalyst [21].

that their removal requires extremely high efficiency at very low concentrations of the bad-smelling substances. Another requirement is quick activation of the catalyst. This can be achieved by the combination of photocatalysts with conventional adsorptive materials, etc. [15,16].

The market of air-cleaners for residential use has seen a rapid growth since 1995, now reaching 1.6 million units per year. Recent products utilize improved light sources as well as long-life and maintenance-free service of photocatalysts, thus making possible a rapidly growing market. Photocatalysts can decompose acetic acid, aldehyde and other chemicals, which cannot be efficiently removed by ozone treatment. Photocatalysts are also used in some vacuum cleaners to remove odors from exhaust air. Current research on photocatalysts is focused on the control of shapes of catalysts and hybridization of functions. Application to textiles will be developed in the near future. For example, titanium oxide particles in musk mellon-shapes (modified $TiO_2$ into porous structure) are studied as fiber additives [17]. Preventing from the direct contact with the textile, titanium oxide particles are coated by porous $SiO_2$.

Noble-metal-based oxidation catalysts are also finding new applications as a result of recent improvements in performance. Matsushita Electric Co. uses platinum-based deodorant catalysts in many of its appliance products [3]. For example, large-size refrigerators which are popular recently are equipped with efficient deodorant catalysts based on platinum-zeolite. Another product using the same catalyst is the kitchen waste processor. Several odorless, kerosine-fueled heaters, cooking stoves and cookers were marketed several years ago, but they were not free from bad smells during the warming-up stage when the catalyst is cold and ineffective. Adsorbents can be used together with catalysts to remove the bad smells. Some using sepiolite for the adsorbent in combination with the platinum catalyst have already been put on the market.

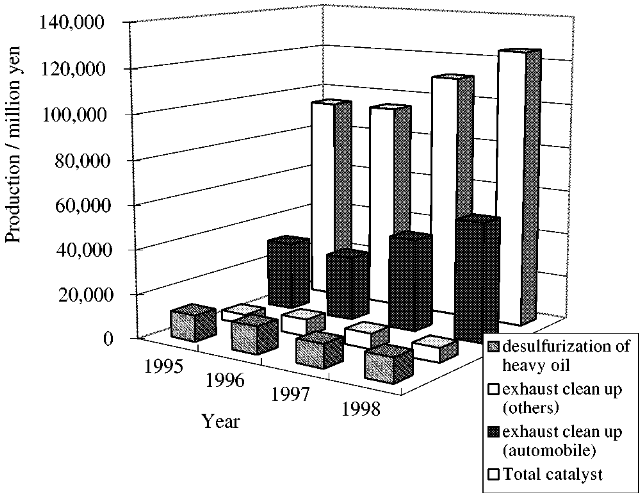


Figure 4. Catalyst production in Japan.

## 5. Cleaning of automotive exhausts from lean-burn gasoline engines

Catalyst production in Japan is steadily growing, reaching 120 billion yen/year in 1998. Figure 4 shows that most of the growth is due to automotive exhaust cleaning, which accounts for 45% of the total, amounting to 54 billion yen/year. When the automotive exhaust-cleaning catalyst was introduced in the 1970s, it was perceived as a temporary solution until the problem is solved by engine innovations. The exhaust-cleaning catalysts, however, are becoming more and more important for removing effectively hazardous components in the exhaust gas from the start of the engine and for a longer service life. Currently the lean-burn engine is a most important technology for better fuel efficiency, but it poses the problem of increased nitrogen oxide in exhaust. GDI (gasoline direct injection) technology also relies on the high efficiency of exhaust-cleaning catalysts.

The catalysts for these purposes are composed of noble metals such as Pt or Pd and alkaline materials like BaO dispersed on $Al_2O_3$ support, and utilize temporary adsorption of reactants onto adsorbent materials. They efficiently absorb and decompose $NO_x$ in the lean-burn exhaust. One type of these $NO_x$ sorption–reduction (NSR) catalysts is used in new model cars from Toyota. This catalyst cleverly utilizes the oxidation–reduction cycle in exhaust, which

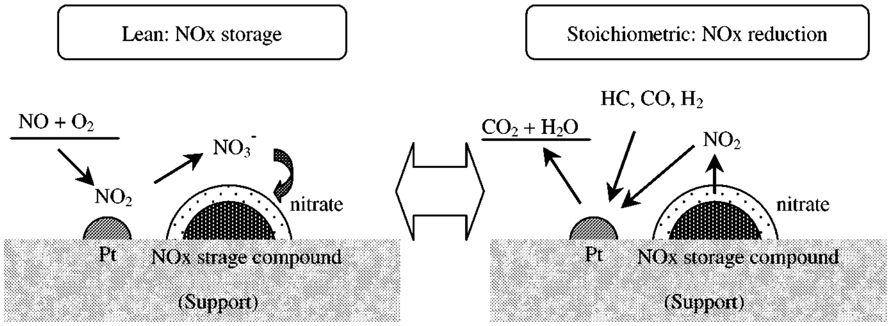
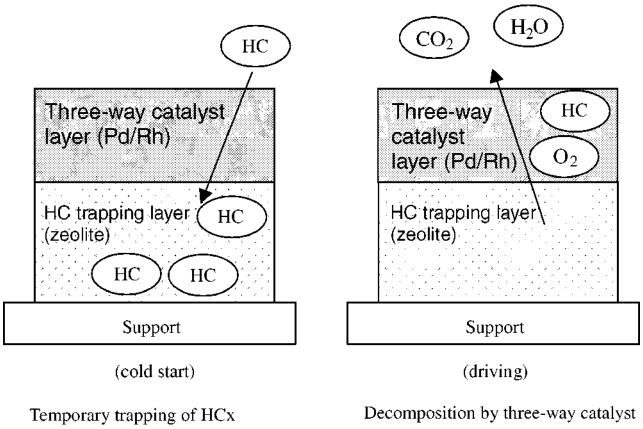


Figure 5. Mechanism of $NO_x$ removal over $NO_x$ storage-reduction (NSR) catalyst [7].



(cold start)

Temporary trapping of HCx

(driving)

Decomposition by three-way catalyst

Figure 6. Mechanism of HCs trapping three-way catalyst (Nissan).

is an adverse phenomenon in conventional catalysts. The catalyst first sorbs $NO_x$ in the form of nitrates under lean conditions, then the nitrate is reduced to $N_2$ under stoichiometric conditions. Thus, it works in adsorption–reduction cycles (figure 5). Toyota seems to plan to use the NSR catalyst as the centerpiece of its exhaust cleaning technology. Toyota has already patented the catalyst internationally and is licensing it to foreign companies.

Meanwhile, Nissan is the first in the world to develop a hydrocarbon-trapping three-way catalyst that temporarily holds hydrocarbons generated during the cold start of the engine. It is installed in the new model of the Cedric/Gloria, turbo-charged version, released in the market last June. As shown in figure 6, the hydrocarbon-trapping three-way catalyst is manufactured by calcining the precursor composed of a three-way catalyst layer, zeolite layer, and support materials. The Pd/Rh catalyst cannot decompose hydrocarbons until the catalyst is heated up to 200–300 °C, releasing hydrocarbons into the atmosphere. Nissan's catalyst temporarily traps hydrocarbons in the zeolite with 0.5–0.8 nm porosity suited for hydrocarbon molecules. When the catalyst warms up, hydrocarbons are released from the zeolite and oxidized by the three-way catalyst to $CO_2$ and $H_2O$.

Honda has also developed an innovative method combining an adsorbent and a catalyst called ZLEV (zero-level emission vehicle). By using this the $NO_x$ level in exhaust becomes even lower than the ordinary urban atmosphere which contains high levels of $NO_x$ and hydrocarbons.

## 6. Developments expected in the near future

### 6.1. Cleaning of diesel exhaust

Requirements for diesel exhaust cleaners are quite severe. Reduction of particulates has been achieved to a certain extent by improvement in combustion technology and developments of oxidation catalyst and trap filters. Recently, "the say No! to diesel vehicles" campaign was initiated by the Tokyo metropolitan government. The new regulations, as shown below, for diesel exhaust will be posed by 2003:

(1) Prohibition of the passage of diesel vehicles not fitted with diesel particle filters (DPF) in Tokyo.

(2) Requirement of the fitting of DPFs to all diesel vehicles registered in Tokyo.

$NO_x$ reduction, however, remains difficult, because the catalyst is poisoned by sulfur in light oil (about 500 ppm in Japan) and the sorption–reduction catalyst described above cannot be used for a long period. The only catalyst system suitable for high sulfur content fuels is a selective catalytic reduction system with ammonia or urea–water. This system has widely been applied for stationary exhaust sources. Recently, the selective catalytic reduction with urea–water using zeolite catalyst has been used practically for exhaust cleaning of Diesel cogeneration systems.

No effective catalyst has been found for mobile exhaust sources. Therefore the only method to remove $NO_x$ from diesel exhaust appears to reduce the sulfur content of the fuel and yet an effective catalyst for $NO_x$ decrease has not been found. Thus novel desulfurization methods for heavy and light oils are eagerly sought. Japan's Environmental Agency and the Ministry of Transportation are planning to tighten the regulations for sulfur content of light oil as low as 50 ppm, one tenth of the current limit, by 2007. The automotive industry, on the other hand, is requesting to reduce the sulfur level of light oil down to 30 ppm or even lower [18]. To achieve this level, however, investment of some 500–600 billion yen is necessary, corresponding to a significant cost increase of 4–5 yen/l-light oil, something for related industries hard to admit. The main process to remove sulfur from light oil utilizes hydrodesulfurization catalyst based on Ni–Mo or Co–Mo. While Scandinavian

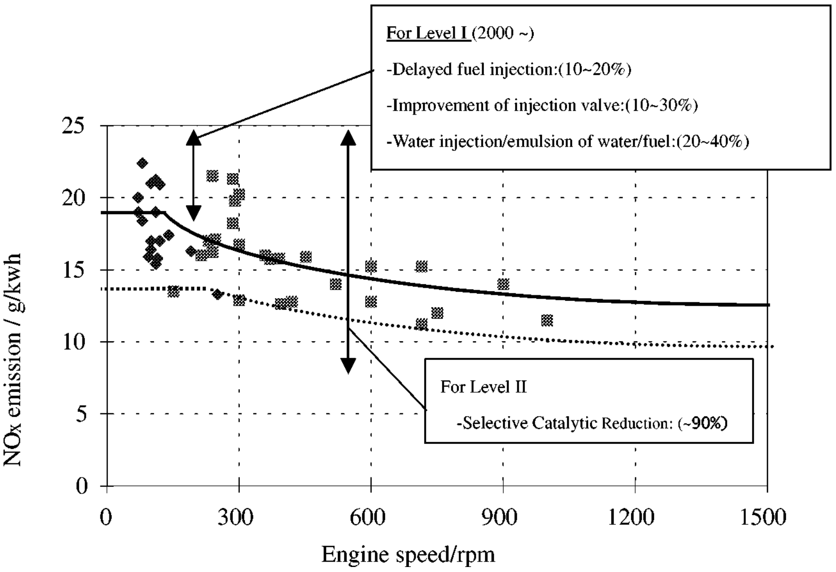


Figure 7. Maximum allowable NO$_x$ emission for marine diesel engines: (——) level I, (· · · · ·) level II, (◆) 2 cycle, and (■) 4 cycle.

nations are trying to reduce sulfur to 10 ppm or less by utilizing this method and lighter crude oil, Japan, relying on Middle Eastern oil with high sulfur contents, must develop a more efficient catalytic desulfurization technology.

Cleaning of exhausts from ships is also becoming an important target. Little attention has been paid to diesel exhaust cleaning of ships. But some reports say that SO$_x$ and NO$_x$ emissions from ocean transportation account for 4 and 7% of global emissions, respectively. To deal with this problem, the International Maritime Organization, at its 41th Marine Environmental Pollution Committee meeting held in 1997, passed regulations for preventing air pollution by ships. Research in Japan is focusing on measures to meet the new regulations to be posed after the year 2000, by the improvements of engine technology such as the delayed fuel injection system as well as the control of its valves (figure 7). These are simple and effective methods, but their effect is limited only to NO$_x$ reduction of ca. 30% at most. Water injection and emulsion fuel systems have been studied, but both suffer from poor fuel efficiency due to low combustion temperature and from corrosion inside the cylinder. To meet the expected tighter regulations (level II), industries absolutely need catalyst technology. Selective reduction by ammonia or urea is a technically established process and has been widely used in NO$_x$ removal for stationary emission sources. Therefore, its application to ships may be quite feasible and its validity has already been tested.

The remaining problems related to its application to mobile sources are:

(1) narrow temperature range,

(2) dealing with variable loads,

(3) cost increase with the use of reducing agent; providing space for reducing agent storage tank.

Therefore, new processes and catalysts that do not need ammonia are being sought. Although selective catalytic reduction of NO$_x$ by hydrocarbons (e.g., propylene) over platinum-zeolite catalyst has been studied, its performance was not good enough. Improvements in the supply of reducing agent and cost reduction are needed. Direct decomposition or selective reduction by particulate or unburned hydrocarbons is a very desirable process, but these all seem to require development of a very new type of catalysts.

### *6.2. Decomposition of dioxin*

Some 80% of the total environmental dioxins in Japan are estimated to come from waste incineration plants. The Japanese government has started to strengthen standards and examine concrete methods to reduce the dioxin level by 90% from the 1997 level over 4 years. Small-sized batch incinerators which generate dioxin because of the relatively low temperature at the start and end of operation, are of particular concern. $V_2O_5$–$TiO_2$ catalyst, which has been widely used for the reduction of NO$_x$ by ammonia, was found effective also in the decomposition of dioxin at around 250 °C and its practical application is being developed.

Meanwhile, Chiyoda Corporation has started a demonstration test for a catalyst that decomposes 90% or more of dioxin at room temperature. This catalyst is placed in a large tank reactor and mixed with a test solution for 1–2 days at room temperature to decompose dioxin. It is designed for practical processing of incinerator ash and polluted soils. The cost is said to reduce by 20–30% as compared with high-temperature catalytic processes.

### *6.3. New application of photocatalysts*

Water processing by photocatalysts is a promising application; but so far only small items such as glassware or drinking water tanks with photocatalyst coatings have been marketed. In contrast, processing of industrial waste water or river water has met technical difficulties due to its large volume, high content of organic matters, and low transparency. Photocatalysts have limited reaction efficiency and decompose trace components only. Therefore, they are used in the last stage of water cleaning in combination with other methods such as membrane filtration or ozone treatment [19].

In this area, new applications are proposed for post-processing. Hitachi Metals Ltd. has developed a new metallic filter bearing $TiO_2$ photocatalyst. Babcock-Hitachi K.K. plans to market a water processor using a photocatalyst which is supported on glass fibers to attain a large surface area by improving the efficiency of the photocatalyst. On the other hand, Adeka Engineering Corporation proposed the combination of aeration and gas phase photocatalytic decomposition of volatile organic compounds such as tetrachloroethylene in underground water and soils. The effectiveness of the photocatalyst is considered to arise from the completeness in chemical reactions that take place at the surface. However, recent reports warn that radicals formed at the surface are released into the vapor phase and that water processing by photocatalysts may form undesirable intermediate chemical species. Also the reaction mechanism has not been elucidated. These aspects must be fully elucidated.

Photocatalysts have been applied to $NO_x$ reduction in ambient air. However, the photocatalyst is basically an oxidation catalyst and converts NO to $NO_2$ which are usually kept on the surface, instead of reducing it to $N_2$. Therefore, the use of this catalyst might lead to more hazardous chemicals. We need more studies to confirm the safety of this material. Efforts are underway to combine the catalyst with a strong adsorbent that holds the $NO_3^-$ species tightly on the surface [20,21].

New research is under way to control the active sites at molecular and atomic levels. For example, the surface of $TiO_2$ photocatalysts, showing superhydrophilicity by ultraviolet irradiation, can be reverted to hydrophobic by visible irradiation [22]. The material showing this hydrophilic/hydrophobic photo-switching is a Cr-doped, $c$-oriented anatase-type titanium dioxide film synthesized by a CVD process. This film, like ordinary titanium oxide film, shows a decrease of water contact angle to about $10^\circ$ when irradiated by ultraviolet light, but subsequent irradation by visible light of 430–800 nm increases the contact angle to $110^\circ$. Subsequent UV irradiation makes the film surface hydrophilic again.

The conventional way of supporting metal particles such as platinum on the surface of $TiO_2$ is to immerse the material in the colloidal solution of metals. This impregnation method usually results in random distribution of metal particles. An alternative method was provided by the photocatalysis of titanium oxide, irradiation of 380 nm laser on $TiO_2$ support film in aq. $H_2PtCl_6$ solution causes reduction of $PtCl_4$ ion to metallic Pt on the plate. The Pt deposition can be patterned on the surface with submicron-order precision by focusing the laser beam. Any shape can be formed by scanning the laser beam on titanium oxide [23].

The effective utilization of solar beam is one of the most important challenges in this field. Development of titanium oxide photocatalysts able to work effectively under visible and/or light irradiation can be considered a breakthrough in efficient and large scale utilization of solar energy. Anpo et al. have improved the photocatalytic properties of $TiO_2$ by the ion-implantation method [24]. The catalyst enables the absorption of visible light even longer than 450 nm. On the other hand, the method of plasma treatment of $TiO_2$ surface (oxygen-deficient-type $TiO_2$) was proposed by Ecodevice Corporation [25]. The demonstration test for the removal of NO by road side painting is in progress.

## 7. Conclusion

Markets related to environment and energy are expected to grow into leading businesses in the next century together with information/communication and electronic technologies. There is a report that estimates the market of environmental catalysts in 2005 to be 2,000 billion yen/year (photocatalyst: 1,100 billion yen/year) [26]. Since chemical reactions usually involve catalysts, developments in catalysts will have significant impact on environmental technology.

Environmental catalysts are increasingly required to have higher performance in order to be useful under conditions much severer than those for the ordinary catalysis for synthetic reactions. Detailed and precise designs are needed to achieve high selectivity for trace substances, which in turn requires clarification of active sites and reaction mechanisms at molecular/atomic levels. As described above, hybridization of several catalytic functions and combination with light and electric stimuli may be a promising strategy. Photocatalysts are already finding wide and novel applications. Diesel exhaust cleaning, on the other hand, remains a challenging field and awaits new breakthroughs.

We expect further progress in environmental catalyst technology to create a more comfortable environment and better quality of life for the future.

## References

[1] M. Iwamoto and H. Hamada, Catal. Today 10 (1991) 57.
[2] T. Nakatsuji and A. Miyamoto, Catal. Today 10 (1991) 21.
[3] A. Nishino, Catal. Today 10 (1991) 107.
[4] M. Misono and T. Inui, Catal. Today 51 (1999) 369.
[5] A. Fujishima and T.N. Rao, Proc. Indian Acad. Sci. (Chem. Sci.) 109 (1997) 471.
[6] M. Misono, Appl. Catal. 129 (1995) N2.
[7] M. Matsumoto, Catal. Today 29 (1996) 43.
[8] TOTO Ltd., wo96/14932 (1996).
[9] Daido Tokushuko K.K., EP 937398.
[10] T. Watanabe, A. Nakajima, R. Wang, M. Minabe, S. Koizumi, A. Fujishima and K. Hashimoto, Thin Solid Films 351 (1999) 260.
[11] K. Shimizu, H. Imai, H. Hirashima and K. Tsukuma, Thin Solid Films 351 (1999) 220.

[12] M. Machida, K. Norimoto, T. Watanabe, K. Hashimoto and A. Fujisima, J. Mater. Sci. 34 (1999) 2569.
[13] R. Wang, K. Hashimoto, A. Fujishima, M. Chikumi, E. Kojima, A. Kitamura, M. Shimohigoshi and T. Watanabe, Nature 388 (1997) 431.
[14] T. Noguchi, A. Fujishima, P. Sawunyama and K. Hashimoto, Environ. Sci. Technol. 32 (1998) 3831.
[15] M. Harada, M. Honda, H. Yamashita and M. Anpo, Res. Chem. Intermed. 25 (1999) 757.
[16] Mistubishi Chemical Corp., JP 08208211.
[17] K. Hayashi, H. Nimura, S. Imaizumi, Y. Sato and N. Yamashita, in: *Proc. 4th Int. Conf. Ecomaterials* (1999) p. 341.
[18] Worldwide Recommendations for Quality Fuels Proposed by Leading Automakers, *Gas and Diesel Quality Key to Vehicle Driveability and Environmental Impact*, Worldwide Fuels Conference, Belgium (1998).
[19] Mazzarino, P. Piccinini and L. Spinelli, Appl. Catal. B 20 (1999) 155.
[20] Y. Murata, H. Tawara, H. Obata and K. Takeuchi, J. Adv. Oxid. Tecnol. 4 (1999) 227.
[21] K. Takeuchi, T. Ibusuki, S.Nishikata and T. Nishimura, *Proc. 2nd Int. Symp. Envir. Appl. Adv. Oxid. Technol.* Vol. 145 (1997).
[22] T. Watanabe, A. Fujishima and K. Hashimoto, 5th Photocatalyst Symposium (1998).
[23] H. Ishii, S. Juodkazis, S. Matsuo and H. Misawa, Chem. Lett. (1998) 655.
[24] M. Anpo, Catal. Surv. Jpn. 1 (1997) 169.
[25] H. Takeuchi, O. Matsumoto, T. Ihara, T. Kondo, H. Okada and S. Sugihara, 5th Symposium on Photocatalysis, Tokyo (1998).
[26] Environmental Catalysts, Research report, Mitsubishi Research Institute, Inc. (1999).