Current Status and Future of the Car Exhaust Catalyst

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1 Introduction

After the elapse of ten years since the beginning of the 21st century, the situation surrounding the car exhaust catalyst - the purification agent of the toxic exhaust gas emitted by automobiles - has come to a critical turning point. Issues such as global warming and environmental hormones feature high on the agenda in the major international conferences attended by the leaders from the nations. In the wake of the September 11 attacks, and the subsequent Iraqi war, the advanced nations, the USA among others, have vied with one another to introduced policies geared for reducing dependency on fossil energy sources. Backed up by the trends toward prevention of global warming and reduction of fissile fuel use, much effort has been in place to develop a variety of automobile technologies such as low-emission, high-mileage cars typically represented by hybrid vehicles, and cars driven by alternative fuels (biofuel). However, the demand for conventional fossil fuel-automobiles seems to be boundless, especially in developing countries such as China and India, and the demand for fossil fuel is projected to increase steadily in the coming 20 years.[1] Car exhaust catalysts in the future need to address two requirements simultaneously: ease of mass production to meet the increasing demand in developing countries, and sophisticated functionality[2] to meet the needs from developed countries.

Since Ford put car exhaust catalysts on the market for the first time in 1970, they have grown into one of the most reliable and stable auto components owing to the sustained effort for improvement and upgrading. However, only the platinum group of precious metals has been used as the catalytically active material during the course of development; no major breakthrough has been made to change this situation for nearly half a century. In the face of the projected depletion of precious metal resources and their possible hike in price due to restricted export from the resource countries, development of new materials and technology is an urgent task for radical reduction of precious metals use. In this report, the author analyses the current status and issues of car exhaust catalyst research and development, and considers the future direction of next-generation catalyst technology that enables radical reduction of precious metal use.

2 Backdrop of Car Exhaust Catalyst

Solid catalysts that have an effect of purifying toxic exhaust emissions from automobile engines are generally called “car exhaust catalysts.” A car exhaust catalyst promotes a series of chemical reactions that clean up toxic gases, normally under ordinary pressure, in the temperature range from 300 to 600°C. The car exhaust catalyst performs continuous processing of the exhaust gas - whose composition changes continuously on a second-to-second basis – and must endure countless oxidation-reduction cycles and mechanical vibration. It is easy to understand the severity of the requirements imposed on the car exhaust catalyst when compared with those counterparts used in ordinary chemical synthesis: the latter is used in a steady condition under which the temperature, pressure, and reactant concentrations are well controlled. The car exhaust catalyst is constantly exposed to the impurities contained in the fuel and corrosive gases originated from lubricant oils, and, depending on the driving conditions, it is exposed to high temperature gas up to 1000°C. Furthermore, unlike other car components, the car exhaust catalyst must operate without any maintenance for several years, or even several tens of years, starting from the car’s start of operation until it retires. This demands an extremely high level of stability and reliability from the catalyst.
The major toxic chemical species (concentration >100 ppm) present in car exhaust emissions include carbon monoxide (CO), nitrogen oxides (NO\textsubscript{x}) and hydrocarbons (HC). In addition to these gaseous chemical species, car exhaust emissions also include a toxic solid matter, i.e. particulate matter (PM). Car exhaust emissions also contain trace amounts (concentration <100ppm) of other toxic chemical species such as sulfur oxides (SO\textsubscript{x}) and phosphorus oxides (PO\textsubscript{x}). Emissions of trace amounts of toxic chemical types does not cause significant physiological and environmental toxicity because of the dilution effect in the air, but they may adsorb on the catalyst surface and act as catalytic poisons, resulting in the reduction of catalytic activity (see section 2-4).

The exhaust emissions from low-emission cars have a different composition from that of gasoline- and diesel-powered cars, but they contain the same major toxic chemical species. The hybrid engine – a combination of a gasoline engine and an electric motor – does not emit exhaust while driven by the motor, reducing the total amount of cruising emissions. In certain high-load situations, however, it emits higher concentrations of CO and HC than conventional gasoline-fueled cars. For example, driving along a sloping road necessitates a frequent switchover between the gasoline engine and electric motor, requiring the gasoline engine to start cold from the standby state, accompanied by a denser emission.\textsuperscript{[3]}

There is a prospect of an increased use of alternative automotive fuels in the future, typically biofuel, which is produced through a biochemical decomposition of biomass. In line with this trend, bioethanol and biodiesel oil are under development for gasoline-fueled and diesel-powered automobiles, respectively. The bioethanol-fueled gasoline engine emits weakly toxic oxides of alcohol (typically acetaldehyde), in addition to CO, HC, and NO\textsubscript{x} with concentrations comparable to those from conventional gasoline-fueled cars. Biodiesel engines emit NO\textsubscript{x} in higher concentration than conventional diesel engines.\textsuperscript{[4]}

For the past several decades, legislative control on the toxic chemical species contained in automobile emissions has been gradually strengthened in many countries in the world.\textsuperscript{[2]} Although the details of the regulation somewhat differ from country to country, major components (CO, NO\textsubscript{x}, and HC) are commonly included in the regulation. In urban areas in Europe and Japan, many of the local governments regulate PM emissions as well. The car exhaust catalyst has evolved steadily responding to the regulatory control with increasing severity.

### 2-1 Toxic Chemical Species in Car Exhaust Emission

<table>
<thead>
<tr>
<th>Toxic chemical species</th>
<th>Physiological toxicity</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC (Hydrocarbon)</td>
<td>Contains carcinogenic components</td>
<td>Benzene (carcinogenic): environmental limit &lt;0.003 mg/m\textsuperscript{3}</td>
</tr>
<tr>
<td>CO (carbon monoxide)</td>
<td>Inhibition of blood oxygen delivery</td>
<td>1,3-butadiene (carcinogenic)\textsuperscript{[4]}</td>
</tr>
<tr>
<td>NO\textsubscript{x} (nitrogen oxides)</td>
<td>NO\textsubscript{2}: breathing disorder</td>
<td>NO\textsubscript{2}: environmental limit &lt;0.04-0.06 ppm/h \textsuperscript{[4]}</td>
</tr>
<tr>
<td>PM (particulate matter)</td>
<td>Breathing disorder, suspected lung cancer-inducibility</td>
<td>Fine particle with a diameter equal to or less than 10μm: environmental limit &lt; 0.10mg/m\textsuperscript{3} (one-day average) AND &lt; 0.20 mg/m\textsuperscript{3} \textsuperscript{[4]}</td>
</tr>
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<table>
<thead>
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</tr>
</thead>
<tbody>
<tr>
<td>HC (Hydrocarbon)</td>
<td>Benzene (carcinogenic)\textsuperscript{a): environmental limit &lt;0.003 mg/m\textsuperscript{3}</td>
</tr>
<tr>
<td>CO (carbon monoxide)</td>
<td>Environmental limit &lt;10ppm/h (one-day average) AND &lt; 20 ppm/h (8-hour average)\textsuperscript{[a]}</td>
</tr>
<tr>
<td>NO\textsubscript{x} (nitrogen oxides)</td>
<td>NO\textsubscript{2}: environmental limit &lt; 0.04-0.06 ppm/h \textsuperscript{[4]}</td>
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2-2 Car exhaust cleanup reactions

The purification reactions corresponding to each of the major toxic chemical species listed in Table 1:

- **CO oxidation reaction**
  \[ CO + 1/2 O\textsubscript{2} \rightarrow CO\textsubscript{2} \textsuperscript{(1)} \]

- **HC oxidation reaction**
  \[ C\textsubscript{y}H\textsubscript{z} + (y+z/4)O\textsubscript{2} \rightarrow y CO\textsubscript{2} + z/2 H\textsubscript{2}O \textsuperscript{(2)} \]

- **NO\textsubscript{x} reduction reaction**
  \[ NO\textsubscript{x} \rightarrow 1/2 N\textsubscript{2} + x/2 O\textsubscript{2} \textsuperscript{(3)} \]

Reactions (1) and (2) are exothermal reactions - a type of combustion - and proceed easily in the
Reaction (4) proceeds relatively easily in the forward direction, because CO and \( C_y H_z \) act as reducing agents.

While a car is running, an oxygen excess condition (lean burn condition) and a fuel excess condition (rich burn condition) come into being alternatively and repeatedly responding to the running conditions; the former favors oxidation reactions, (1) and (2), and the latter favors reduction reactions, (3) and (4). The car exhaust catalyst can only demonstrate its maximum performance in a narrow range of component composition, which is realized when lean burn and rich burn conditions change places (Figure 1) The superb level of exhaust emission control attained by the present-day car exhaust catalysts mainly owes to the advanced electronic fuel control system; it controls the air-fuel ratio based on the real-time feedback information of emission composition so that emission with an optimum composition is delivered into the engine.\(^6\)

With regard to the purification of NO\(_x\), a separate reaction is known, besides (3) and (4), that takes advantage of an addition of nitrogen-containing reducing agents (e.g. ammonium, urea) \textit{ab extra} into the reaction system.

\[
\text{NO}_x + 2x/3 \text{NH}_3 \rightarrow (1/2 + x/3) \text{N}_2 + x\text{H}_2\text{O} \quad (5)
\]

The nitrogen-containing reducing agent has the merit of being capable of NO\(_x\) selective catalytic reduction (SCR) even in the co-presence of oxygen.
The need for a dedicated reservoir, however, makes this scheme difficult to apply in small cars. It is almost exclusively used in large diesel engines.

For particulate matter (PM), no effective purification reactions or catalytic materials have been brought into practical use up to now. PM is removed from the emission flow physically by means of a dust filter. See references[5] and[7] for a detailed description of purification technologies for diesel engine emission and PM.

As is detailed in the next section, the car exhaust catalyst consists of precious metal nano-particles dispersed and supported on the surface of oxide supports. As the precious metal nano-particles exhibit catalytic activity to many physiological reactions, there is a concern about intaking collapsed catalyst particles (precious metal combined with support debris) along with inhaling emission gas, which may trigger certain diseases as the intake of PM does.

2-3 Materials and configuration of car exhaust catalysts

The car exhaust catalyst has a composite structure consisting of transition metal nano-particles or transition metal ions dispersed and supported on the surface of a support material, which is either microparticles with a very large specific surface area (normally > 100 m²/g) or a highly porous matrix. The mainstream car exhaust catalyst has a configuration wherein a platinum group precious metal - such as platinum (Pt), palladium (Pd) or rhodium (Rh) – is dispersed as the catalytic center on the surface of a refractory oxide support that usually has silica (SiO₂), alumina (Al₂O₃) or ceria (CeO₂) as the main constituent. The configuration is called a three-way catalyst (TWC). In addition to the support materials cited above, refractory alumino-silicate materials, typically cordierite (2MgO:2Al₂O₃:5SiO₂), are also used as the oxide matrix.

2-4 Technical challenges of material

The prime requirement for the materials used in a car exhaust catalyst is a very high level of heat resistance and to ensure stability and reliability in long-term service. Catalytic centers of the car exhaust catalysts are, at ordinary temperatures and pressures, in a high dispersion state on the surface of supporting materials (Figure 3a). However, at higher temperatures (≥ 300°C) at which the catalyst functions, catalytic centers become massed together, or agglomerated, and the effective surface area decreases, resulting in a gradual degradation of overall catalytic functions with time. In practical car exhaust catalysts, a large excess of catalytic centers are normally dispersed on the support material surface to compensate the dwindling catalytic functions due to agglomerated catalytic centers. This translates into a larger consumption of precious metal than is actually needed.

The second challenge placed on car exhaust catalysts is the upgrade of resistance to catalytic poisons, typically SO₂. The surface of metallic nano-particles, or the catalytic center of car exhaust catalysts, often shows affinity to other chemical species than the target reactive species of the catalyst. Notably, the palladium (Pd) surface chemically adsorbs sulfur dioxide (SO₂) strongly. In case SO₂ is present in the exhaust gas, a stable SO₂ adsorption layer is formed on the catalyst surface and the layer blocks other chemical species from adsorbing on the surface, resulting in a serious suppression of the desired exhaust purification reactions (blocking layer, Figure 3b). This phenomenon is called catalyst poisoning.[8] In actual car exhaust catalyst systems, the catalyst material is overheated at regular intervals to promote thermal desorption of the catalytic poisons from the catalytic center surface, for reactivation of the catalytic function. This process, however, contributes to a vicious cycle: the overheating treatment enhances thermal agglomeration of catalytic centers.

The third challenge presents the highest hurdle of all. Platinum group precious metals – primary material for producing car exhaust catalysts – are characterized by small market circulation volume, and are plagued with wild fluctuations in price. These precious metals are representatives of the so-called “rare” metals, and more than 90% of their global output comes from the top three producing countries.[9,10] Because of the extreme maldistribution of the mineral resources, the rare metals pose a constant risk to the stable supply of these resources: changes in political situations in the producing countries may result in a constrained supply of raw materials. Notably, rhodium (Rh) is associated with the highest risk of this kind. It is practically the only one catalytically active material for the use in NOx reduction reactions, and its applications are almost exclusively targeted to the car exhaust catalyst (Figure 4). Still, its output is very

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Figure 3: Thermal agglomeration a), and catalyst poisoning b), of the catalytic center of car exhaust catalysts

Figure 4: Applications of precious metals (from: Johnson-Matthey Platinum 2009)

Figure 5: The components distribution in precious metal deposits (from: Johnson-Matthey Platinum 2009)
small (a tiny amount is produced as a byproduct of Pt and Pd; Figure 5). Amid the global trend promoting technical development conducive to usage reduction and recycling of rare metals, the ultimate and most sought-after technical challenge is the realization of a rare-metal-free car exhaust catalyst.

3 Research & Development of Catalyst Materials

From the beginning when the car exhaust catalyst first came into use, several issues have been under research as persistent technical challenges typically including reduction of precious metal use and improved performance. The reduction of precious metal use – and ultimately a complete elimination of its use – contributes to lower material cost and stable supply, and the performance improvement includes a simultaneous pursuit of higher catalyst poison resistance (e.g. against SO\(_2\)) and superior thermal resistance, or prevention of thermal degradation through the overheating process. Complete solutions to these issues are still not available. We can point out the difficulty of identifying materials for car exhaust catalysts, and the difficulty of analyzing catalytic reaction mechanisms as the major obstacles standing in the way of finding solutions.

3-1 Research history up to the present

Major experimental methods employed in the research areas relating to exhaust catalysts are summarized in Table 2, along with a schematic diagram showing the time evolution of the research areas. Synthesis of practical catalysts has been conducted, since the 1970s up to now, using inorganic and organic chemical synthesis techniques such as the precursor reduction in solution. Meanwhile, from the 1970s through the 1980s, spectrochemical techniques such as X-ray absorption near-edge structures (XANES) and infrared spectroscopy (IR) were the main tools for identifying catalytic materials and analyzing catalytic reactions. All these synthesis methods and spectrochemical techniques followed in the footsteps of those established for the development of catalytic systems such as the Ziegler-Natta catalysts (titanium-chloride catalysts used in polyethylene synthesis) and zeolite catalyst (alumino-silicate catalyst used in olefin cracking). These catalytic systems have a common feature: they have either atomic or ionic catalytic centers (Figure 6a).

However, unlike in the cases of zeolite catalyst and others, the catalytic centers of car exhaust catalysts are neither atoms nor ions, but nano-sized particulate solids (Figure 6b). Nano-sized particulate solids are generally too small for a diffractometric identification technique, such as X-ray diffraction (XRD), and are too large for identification using a spectrochemical technique. Different from the cases with atoms and ions, a solid surface often exhibits complicated and unpredictable behavior involving a dynamic rearrangement of atomic arrays as the reactive chemical species adsorb on it. Conventional analytical chemical techniques were applicable to neither the identification of the nano-sized catalytic centers nor the analysis of catalytic reactions.

Surface science, which showed rapid growth in

<table>
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<th>Table 2: Major experimental techniques used in car exhaust catalyst related areas, and their evolution with time</th>
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<tr>
<td>Material synthesis</td>
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<td>Research &amp; development of practical catalysts</td>
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<td>Nano-measurement</td>
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the 1980s and reached a stage of technical maturity in the early 1990s, elucidated the catalytic reaction processes taking place on solid surfaces one by one. Above all, the successful real-time observation of catalytic reaction processes by photoelectron emission microscope (PEEM) was an epoch-making achievement.[10] It is to be noted, however, that all of the surface scientific analysis techniques, including PEEM, were developed to analyze clean solid surfaces prepared under ultra-high vacuum conditions (Figure 6c). Actually, all car exhaust catalysts are operated under exposure to atmospheric pressure. It is not realistic to assume that the catalytic centers on car exhaust catalyst surfaces have equivalent characteristics as those on clean surfaces prepared under an ultra-high vacuum. Therefore, the reach of the contributions from surface science in the 1990s was limited for the true understanding of actual catalytic reactions.

A series of breakthroughs was brought about in the middle of 1990s and later when the nano-technological methodology came into widespread use globally. In this period, the emergence of nano-measurement tools had a huge impact on surface science and the research & development of practical catalysts. The tools notably included scanning transmission electron microscopy (STEM), and the photoelectron spectroscopic methods (XPS/UPS) based on the use of synchrotron radiation. Especially, STEM provided a revolutionary analytical means in that it could determine the crystal structure and the chemical composition at each catalytic center. At present, STEM has gained such an identification capacity that it provides the atomic number for each constituent atom of a nano-sized particle.[13] Photoelectron spectrometry used to prove effective only for clean surface analysis, but the advent of synchrotron XPS has extended the reach of this technique far beyond the conventional range, including chemical state analysis of actual catalytic centers dispersed in the support material. Since identification of catalytic centers became available at the atomic level, the gap between surface science and the research & development of practical catalysts narrowed rapidly.

The progress described above is well exemplified when we take a look at the trend of research themes published in these 40 years, since the advent of the three-way catalyst. Figure 7 shows a statistical frequency analysis of the methods employed, for material identification and elucidation of catalytic reaction mechanism, in the papers that related directly or indirectly to the car exhaust catalyst. Two types of catalysts were compared – car exhaust catalysts with nano-particulate catalytic centers and a conventional catalyst – a zeolite catalyst with ionic catalytic centers was used for the latter as reference. In this investigation, searches were made on the article subjects and abstracts using the scholarly journal article database SCOPUS, where keywords such as “(Pt+Rh+Pd) × (catalyst) × (sample identification and catalysis reaction analysis method (UV, IR, etc.)” were used for searching papers relating to car exhaust catalyst, and “zeolite×catalyst × (sample identification and catalysis reaction analysis method)” was used for searching articles relating to the zeolite catalyst. The articles that met the search conditions were extracted, and the result was plotted with the methods (material identification and catalysis reaction analysis) on the horizontal axis, with the number of articles corresponding to them plotted on the vertical axis.

The search result on articles relating to car exhaust catalysts showed that, during the 20-year period from 1969 to 1989, spectrochemical methods, typically IR, dominated in the material identification and catalytic reaction analysis (Figure 7, white boxes in the left chart). Since 1990, STEM/TEM and XPS/UPS methods became by far the most frequently used method (Figure 7, black boxes in the left chart). For the reference subject (i.e. zeolite catalysts), in contrast, no significant difference was found between the two periods – from 1969 to 1989, and 1980 or later (white and black boxes in the right chart). This result shows very clearly that the nano-measurement tools had a huge impact on the car exhaust catalyst research, where the surface of nano-solid particles plays an important role as catalytic centers.

A research example in the field of car exhaust catalysts where a nano-measurement tool had a decisive contribution to solving the technical challenge was the research & development of an intelligent catalyst published in 2002.[13,14] The material used in the intelligent catalyst is a perovskite-type composite oxide with the composition formula \( \text{AB}_{1-x} \text{PGM}_x \text{O}_3 \), which is stable at normal temperatures and pressures. In this formula, \( A \) represents a lanthanoid or alkaline earth element, and \( B \) a 3d-transition metal, and \( PGM \) a precious metal, respectively. When exposed to a reductive gas atmosphere that contains CO and HC,
the material segregates into two distinctive phases—a deficient form of oxide and pure PGM phases—by releasing PGM ions out of the crystal lattice. The pure PGM phase precipitates on the surface of the oxide matrix as nano-particles with a size of roughly 1nm, and it exerts purification activities for car emissions. As described in section 2-2, two air-fuel conditions take turns repeatedly inside an automobile— the rich burn condition (excess amount of CO, HC; reductive atmosphere) and the lean burn condition (excess amount of NOx, O2; oxidative atmosphere). The pure PGM nano-particle phase, once deposited under exposure to reductive atmosphere, is oxidized to ions again when the emission changes to oxidative atmosphere and dispersed inside the perovskite lattice. This repetitive creation and annihilation of catalytic centers in sync with the reductive/oxidative atmosphere cycle have an effect of preventing the agglomeration of catalytic centers. This also enables a drastic reduction of precious metal use, as well as realizing superb heat-tolerance characteristics.

The intelligent catalyst is an achievement of researchers in private enterprises, who endeavored through much trial and error to upgrade the heat resistance property, no matter how slight a degree, of the catalytic centers of three-way catalysts (Pt, Pd, or Rh nano-particle) by dispersing them on a variety of oxide supports. During the course of research & development, samples were sent to SPring-8 (a Japanese synchrotron radiation facility) for high-intensity source EXAFS analysis. The analysis revealed that the catalytic centers are created and annihilated repeatedly depending on the changes...
in atmosphere – a mechanism of catalysis peculiar to the intelligent catalysts.\[15\] The analysis not only indicated an excellent solution against the thermal agglomeration of catalytic centers – one of the greatest challenges remaining in the three-way catalyst – but also provided groundbreaking knowledge on the behavior of metallic ions inside the oxide matrix exposed to a changing atmosphere. The intelligent catalyst can be viewed as an outstanding success example, where collaboration of material development and nano-measurement technology had a significant contribution both on basic and applied research & development.

3-2 Trends of research & development in the future

Although the development of the intelligent catalyst brought us a breakthrough upgrade of temperature resistance, in precious metal-based car exhaust catalysts, challenges with greater difficulty still remain: a precious-metal-free catalyst that totally eliminates the use of precious metals, and catalysts resistant to poisoning by impurities. Toward the realization of precious-metal-free catalysts, many attempts are being made to use nano-particles produced from non-precious metal-based alloys (e.g. Ni or Fe) as catalytic centers. Recently, coverage became a focus of attention that reported that a carbide alloy catalyst – a combination of carbon, iron, and cerium – exhibited an emission purification activity better than the platinum-based catalysts.\[16\] The reported catalyst deserves attention not only because it indicates the realization of a precious-metal-free catalyst, but also because it uses iron, an element without physiological toxicity, as a constituent. At present, detailed information on this material is not available. The future success of identification in such key items as the chemical composition and the crystal structure of the catalytic centers, morphology and sizes of the catalyst can well bring about a significant breakthrough both in terms of basic science and the development of practical materials.

The precious-metal-free catalyst must have a high level of resistance to impurity poisoning, as well as an emission purification performance equal to, or better than that of precious-metal-based counterparts. Even if suffering poisoning from such material as SO\(_2\), the precious metal catalyst can be reactivated through an overheating process that thermally desorbs the catalytically poisonous materials. Because of this property, a higher emphasis was placed on improved thermal resistance rather than on resistance to impurity poisoning in the development efforts of three-way catalysts. If the transition to precious-metal-free catalysts, with base metal elements in the catalytic center, succeeds in the future, there will be a concern that the catalytic center may be transformed into sulfides and/or phosphides, resulting in irreversible deactivation of the catalysts.

Several attempts are being made at present to improve the poisoning resistance of metallic catalysts. An attempt has been reported, for example, to combine the catalytically active element with other metallic elements; the combination transforms the catalytic center into an intermetallic compound – neither a metallic element nor an alloy – that sterically blocks surface absorption of catalytic poisons.\[17\]

Another research group is trying to use cobalt ions and/or copper ions incorporated in zeolite and aluminum phosphate lattices as a catalytic center, instead of conventional metallic nano-particulate catalytic centers. The group has so far succeeded in producing a good NO\(_x\) reducing characteristic using this system.\[18\]

Although these attempts are still in their basic research stages, expectations are running high that they will evolve, with the help of closer collaboration between nano-measurement technology and surface science, into practically feasible new catalysts in the future.

4 The Research System in the Future

Research on the elementary processes of car exhaust catalysts has been propelled energetically worldwide by the academic communities, notably universities and national research organizations. The Nobel Prize in Chemistry in 2007 was granted to the research on dynamic adsorption and desorption processes of carbon monoxide and oxygen on solid surfaces.\[19\] On the other hand, the evolution of car exhaust catalysts for practical use owes much to the research & development effort of individual car manufacturers. Starting with the development of the three-way catalyst (Ford; see 2-3), many achievements followed suit, from the realization of the NO\(_x\)-trap catalysts (TOYOTA) until the recent development
of the intelligent catalyst (DAIHATSU[13-15], see this report). The NO\textsubscript{x}-trap catalysts enhanced catalytic response following the changes in air-fuel ratio by addition of alkaline-earth elements to the three-way catalyst, and the intelligent catalyst improved heat resistance dramatically by utilizing phase separation phenomena in precious metal oxides. It is safe to say that all of the major innovation in this field came from car manufacturers, especially from Japanese manufacturers.

For Japan to maintain and extend its competitive edge in this area, neither the industrial sector-driven research & development for practical materials nor the basic research in academic communities will be sufficiently effective in itself in a view toward the future. A constructive cyclic relation should be established between them: knowledge of the reaction mechanism obtained from basic research and the design proposals of catalytic materials will be reflected in the research & development of practical materials without delay, and the new catalytic materials and processes developed in the industrial sector will provide novel research subjects.

For this purpose, as the success case of the intelligent catalyst indicates, it is essential for the industrial sector and academic community to collaborate closely to carry out a two-way approach, i.e. basic and applied research concurrently, taking full advantage of the nano-measurement tools. In concrete terms, active use of the following advanced experiment equipment is essential: high-performance scanning electron microscopes (identification of nano-particulate catalytic centers at an atomic level), photoemission spectroscopy (e.g. SPring-8; elucidation of catalysis). In addition, proactive use of supercomputers is also indispensable – it sheds new light on surface reaction dynamics from the theoretical viewpoint. Many of these tools require a high level of investment for introduction and operation, and also require both the knowledge and experience on the part of the user to operate such sophisticated instruments and to perform highly complex data analysis. Especially, to take full advantage of the supercomputer, the requirements go far beyond the high-speed central processing unit and huge storage capacity: the development of mathematical models and software with superior general versatility and analytical performance will be an integral part of the system use, and the model must be able to incorporate such information as the catalyst material’s structure, composition, and catalytic characteristics as extensively as possible.

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