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Recent progress in the practical applications of heteropolyacid and perovskite catalysts: Catalytic technology for the sustainable society

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ABSTRACT

Recent progresses in practical applications of (i) supported heteropolyacid and (ii) Pd/perovskite catalysts are described. (i) Two industrial catalytic processes, ethyl acetate and acetic acid syntheses both from ethylene, utilize silicotungstic acid, alone and together with Pd, respectively, carefully supported on silica, and exhibit high performance from green chemical and economical viewpoints. The layer structure of heteropolyacid on silica and physical properties of silica are among the key factors of the high performance. (ii) Pd/perovskite catalyst is applied for the treatment of automotive emission, where the catalyst life is very much elongated by embedding Pd into the perovskite lattice and hence resulted in much reduced usage of Pd. These are good examples of green catalytic technology that will contribute to the sustainable society.

1. Introduction

In this article, progresses in practical applications of heteropoly and perovskite catalysts since the previous review about the same classes of catalysts (Catal. Today 100 (2005) 95) are briefly reviewed. These two types of catalysts (heteropoly and perovskite) have been the main subjects of our research aiming at the design of practical catalysts based on structurally well-defined mixed oxides. Moreover, the applications of both catalysts fit the idea of green and sustainable chemical technology.

1.1. Green and sustainable technology

Catalysts are indispensable tools for the green and sustainable chemical technology, but are meaningful only when they are beneficially used in practical applications. In other words, catalytic technology can be a key technology for the sustainable society only by demonstrating its usefulness in the society by the improvements of human welfare and the environment. In this respect it is regrettable that there have recently been very few novel innovations having posed a great impact on the society. In the present article, the successful efforts made by the Japanese companies in collaboration with academia will be described, where heteropolyacid and perovskite catalysts (see Fig. 1) were used to develop chemical processes that are green and sustainable. Even though the achievements may not be very great, the author believes that continuing efforts to innovate practically useful catalysts are very important for the progress of catalytic science and technology.

Consider the following simple equation that always holds:

$$\text{Environmental Impacts or Chemical Risks (EI or CR)} = \{(\text{EI or CR})/(\text{GDP})\} \times (\text{GDP/Population}) \times (\text{Population}) \quad (1)$$

For the suppression of the left hand side of the equation, namely, environmental impacts, EI, or chemical risks, CR, it is necessary to reduce the first term on the right hand side of the equation, that is, (EI or CR)/(GDP), where GDP = Gross Domestic Production = human economical activities, because the second and third terms on the right side, (GDP/Population) and (Population), will continue to grow in the future particularly among developing countries. So-called Environmental Kuznets Curve represents essentially the same idea, where EI or CR [ordinate] is plotted against GDP/Population [abscissa] and an inverse U-type curve (initially upward, but downward in the later stage) is expected.

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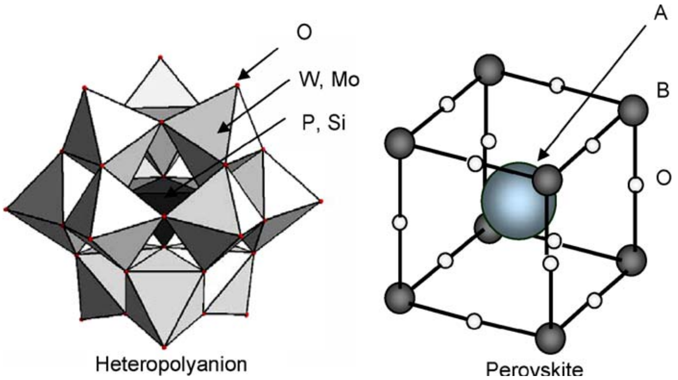

Fig. 1. Heteropolyanion structure (Keggin-type polyoxometalate anion) and perovskite unit cell (ABO_3, cubic).

As the economy grows, (EI or CR) increases in general concurrently with GDP/Population, or the living standards. Developed countries attempt to separate the two axes, (EI or CR) vs. (GDP/Population), and make a U-turn in the curve (to the downslope of the curve). NO_x and SO_x emissions, for example, tend to show the U-turn by applying regulations and technical measures, but the emission of CO_2 in most developed countries still continues to rise, in spite of various efforts. In developing countries, all of these are sharply growing.

Green Chemistry is defined by the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products [1], where precautionary efforts made at the design stage are stressed rather than end-of-type treatments. The term, Green Chemistry (GC), was first introduced in US in the 1990s, but the idea of Green Chemistry is not new and there were many early examples in line with this idea.

There are quite a few good examples in Japan, as well. One of the examples is shown in Fig. 2 [2]. This is about the emission of BOD (biochemical oxygen demand), or organic waste, into rivers. In 1970, the total amount of the BOD emission was 3.75 million tons, most of which is from industry and the half of it from pulp and paper industry. In about 20 years it dramatically decreased to less than one million tons by the efforts principally made by the industry, including the paper and pulp industry. The decrease realized by the pulp and paper industry, in spite of increased production, was mostly due to the change of the process (from sulfite pulp to kraft pulp) and raw materials (increased usage of recycled paper), and the waste water treatment contributed to only 15% of the decrease. Thus this is an excellent example of Green Chemistry accomplished before 1990.

Another good example of green chemical technology developed in Japan is the electrolysis of NaCl using an ion-exchange membrane. After many technological improvements, the process is now the greenest and most efficient process.

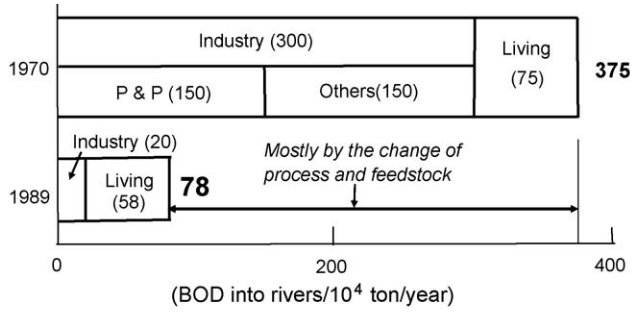

Fig. 2. An example of green chemistry before green chemistry. BOD emission into rivers in Japan.

1.2. Green catalysts and environmental catalysts

If one looks at catalytic technology for the sustainable society, its roles may be two ways: (i) green catalysts that realize green chemical processes, that is, environmentally friendly and non-hazardous processes, and (ii) environmental catalysts that eliminate or diminish hazardous compounds, including so-called end-of-pipe technology. These two are to be developed for the suppression of (EI or CR)/(GDP) of Eq. (1).

In this article, as an example of green catalysts, *heteropolyacid catalysts* will be described and, for environmental catalysts, *perovskite catalysts*. The author's group has studied many years fundamentally the catalyst design based on well-characterized, namely, crystalline or molecular mixed oxides. Heteropolyacids and perovskites are the examples and the major materials we studied. In addition, both were developed successfully for practical applications by industry (Showa Denko and Daihatsu, respectively) in collaboration with the author's group: (1) improvement of the performance of supported heteropolyacid catalysts for the productions of ethyl acetate and acetic acid both from ethylene, and (2) improvement of catalyst life of automotive three-way catalyst by using a combination of noble metals and perovskite. The former made the processes much greener and more profitable, and the latter resulted in dramatic decrease in the amount of usage of noble metals: Pd, Pt and Rh.

2. Heteropolyacid catalysts

Catalytic chemistry of heteropolyacids has been reviewed by several groups [3] and there are already several industrial processes utilizing heteropolyacid catalysts [4]. In relation to the catalyst improvements described in the present article, the concept of three distinctly different types of catalysis present for solid heteropolyacids was important. In particular, the surface acidity and moderate (not too much) contribution of pseudo-liquid catalysis was essential.

As for the heteropoly compounds in the solid state, we have demonstrated from the late 1970s that the solid structure must be understood hierarchically. The primary structure is the molecular polyanion (here, Keggin anion). The secondary structure is three-dimensional crystal of the polyanions and various cations. The tertiary structure is the assembly of the secondary structure, for example, resulting in different particle size and pore structure. Flexible nature of the secondary structure of certain heteropolyacids is the origin of pseudo-liquid catalysis, one of the three types of catalysis of solid heteropolyacids [3a–c].

2.1. Supported heteropolyacids

We have studied mostly unsupported heteropolyacid catalysts, but there have been several studies on supported catalysts including ours [5]. The necessity of supported heteropolyacids in practical applications is evident from the examples described below. We found a very high catalytic activity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, so-called Cs2.5, for various surface-type reactions. The reason of the high activity was essentially due to its high surface acidity brought about by its high surface area, in addition to the high catalytic activity of the surface acidic proton. The surface area of Cs2.5 is very high (100–200 m^2/g), because Cs2.5 consists of aggregates of very fine particles. As Cs salts have uniform composition in the solid after heat-treatment, it is possible to estimate the number of protons on the surface from the chemical

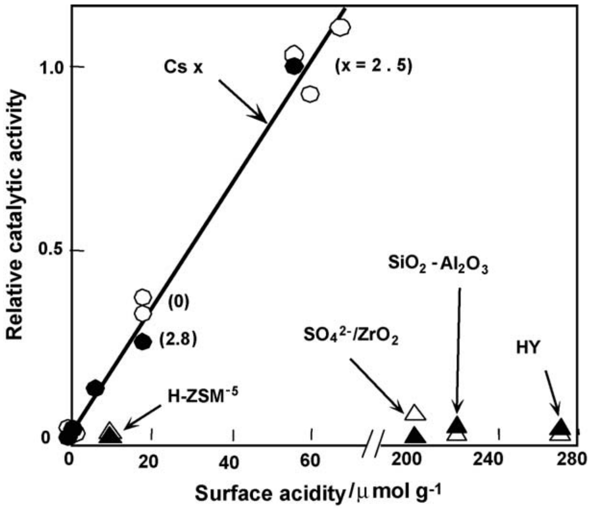

Fig. 3. Plots of the catalytic activity for alkylation of aromatic compound as a function of the surface acidity (number of surface protons) for $Cs_xH_{3-x}PW_{12}O_{40}$ (Cs, *x*) and the conventional solid acids [3b].

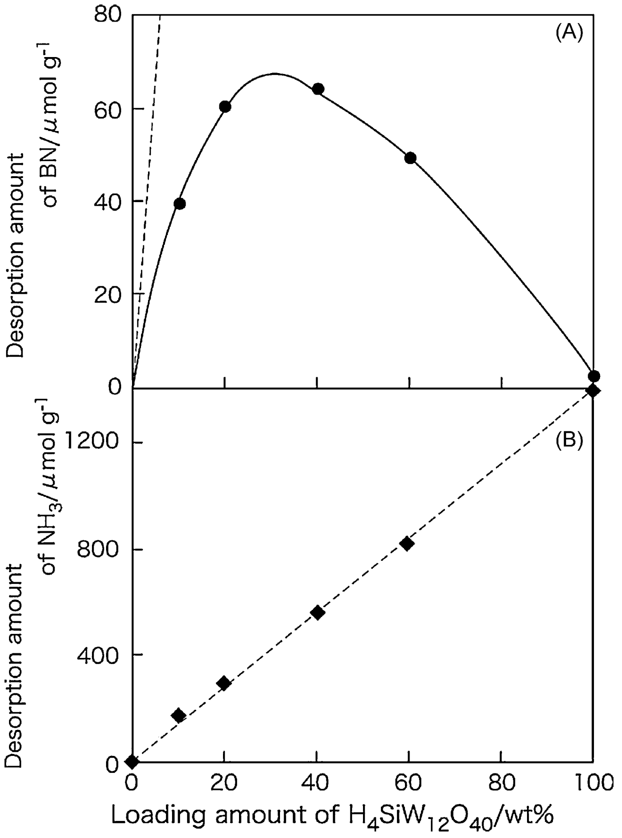

Fig. 4. Surface acidity measured by BN-TPD (top) and bulk acidity measured by NH_3-TPD (bottom) of $H_4SiW_{12}O_{40}$ supported on silica [6,7].

formula and the surface area. The catalytic activity is linearly plotted against the number of protons on the surface (surface acidity) thus calculated, as shown in Fig. 3. Another important point to be noted in this plot is that the catalytic activity per surface proton of heteropolyacid (the slope of the linear plot) is much greater than the proton of the conventional solid acids plotted in the same figure.

What this linear plot indicates is that, if heteropolyacids including acid forms having very small surface area (several m^2/g) are adequately dispersed on supports that possess a large surface area, they would exhibit a very high catalytic activity and find wide practical applications. Note that heteropolyacids containing elements such as Cs and W are more expensive than support materials, and most unsupported heteropolyacid powders are not mechanically strong enough for practical solid catalysts.

Okuhara and co-workers [6,7] developed a method to measure the surface acidity of heteropolyanion with temperature programmed desorption (TPD) using benzonitrile (BN). Since BN adsorbs only on the surface, BN-TPD can measure the surface acidity. If ammonia is used for TPD, as ammonia is absorbed into the solid bulk of most heteropolyacids, the acidity measured is “bulk” acidity and increases almost linearly with the amount of heteropolyacid loaded, as shown in Fig. 4 (bottom).

Fig. 4 also shows the change of surface acidity measured by BN-TPD when the amount of heteropolyacid loaded on silica increased. At a very low loading level (<5 wt%), strong acidity attributable to heteropolyacid was hardly detectable, and upon an increase in the loading level the acidity gradually increased, but at the loading level of 15–50 wt% the surface acidity showed plateau and then declined (>50 wt%). From this figure, it may be speculated that at a very low loading level heteropolyacid exists as a monolayer or small islands on the support, where some of polyanions decompose or change their chemical properties by strong interactions with the surface of support. With increasing loading level, the layer gradually becomes thicker or islands become larger and broader, and there are 3–6 layers at 15–40 wt%. Above about 60 wt%, heteropolyacids form thick layers and/or larger crystallites. These changes are schematically illustrated in Fig. 5. Note that the surface acidity is much lower than the bulk acidity in quantity.

The above speculation is consistent with the IR and XRD observation. IR bands characteristic of Keggin anion were found above 10–20 wt% loading. At lower loading levels, some Keggin anion may exist without decomposition and would be detected, if the sensitivity allows. Broad XRD lines attributable to the bulk heteropolyacid (cubic) (*secondary structure* in this case) were detected above about 50 wt% loading, indicating that the crystal size of heteropolyacid became large enough for XRD detection.

The supported heteropolyacid catalyst having the highest acidity was applied for a reaction that involves both alkylation and acylation [6,7]. As expected, the catalyst showed a much higher activity than the conventional solid acids, although some deactivation was observed upon repeated usage of catalyst.

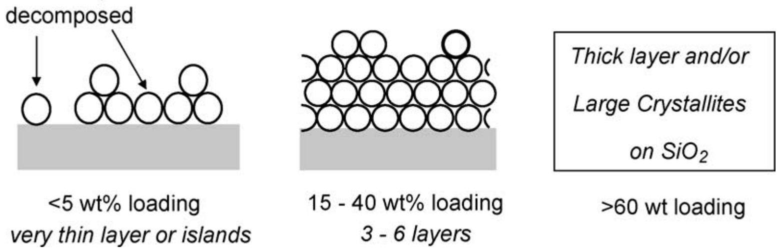

Fig. 5. Schematic models of the layer structure of $H_4SiW_{12}O_{40}$ supported on silica.

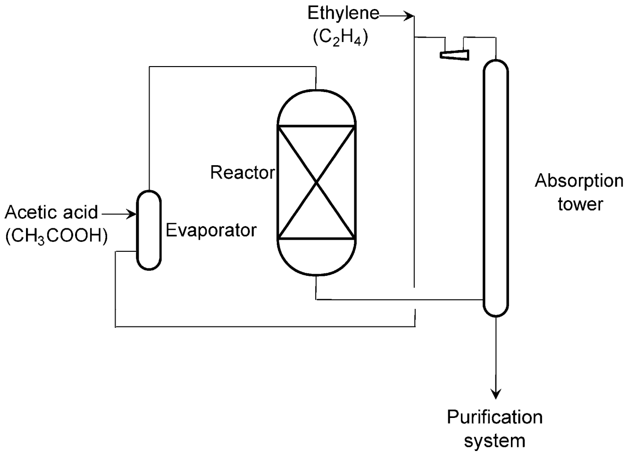

Fig. 6. Flow chart of ethyl acetate plant.

We, the groups of Showa Denko, Hokkaido University and the author, attempted to improve the two catalytic processes that had been industrialized in 1997 and 1998, respectively, by applying the knowledge as described above, since both processes were more or less suffering from serious catalyst deactivation.

2.2. Synthesis of ethyl acetate from ethylene and acetic acid

First example is the synthesis of ethyl acetate from ethylene and acetic acid using solid acid catalysts.

$$CH_2{=}CH_2 + CH_3COOH \rightarrow CH_3COOC_2H_5 \qquad (2)$$

This reaction has several advantages from the green chemical viewpoint, as described later, but the conventional solid acids showed very low catalytic activities (note that, if ethanol is used in place of ethylene, ethyl acetate is easily obtained with the conventional acids). In contrast, Cs2.5 described above exhibited a high activity close to the targeted value. After several trials and errors, a good performance was obtained by using a heteropolyacid supported on silica. The process was industrialized by Showa Denko in 1998.

Fig. 6 shows a simplified flow chart of the process. In the real plant, however, rather rapid deactivation of catalyst took place and, therefore, a much longer catalyst life was necessitated from the economical viewpoint. So we started the collaboration to solve the problem.

Several successful improvements of the process we accomplished are summarized in Fig. 7.

1. Structure of supported HPA → appropriate thickness of HPA layer
   (thick layers → pseudo-liquid → oligomerization)
2. Impurity of silica → elimination of Al, Fe, etc.
3. Physical properties of silica
   → high surface area and uniform pore size (ca. 5 nm)
4. Addition of steam into the feed and precise control of its partial pressure
5. Operation conditions → uniform distribution of temperature

Fig. 7. Major improvements made to achieve high performance of the new ethyl acetate process.

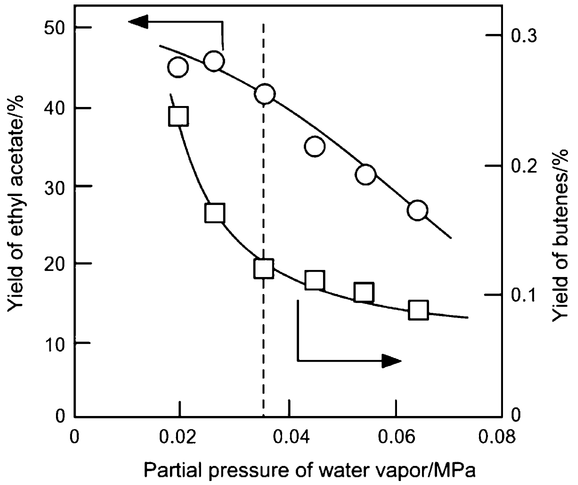

Fig. 8. Dependencies of the yields of ethyl acetate and butenes as a function of partial pressure of water vapor.

First, the mechanism of deactivation was thoroughly examined and it was found that the main reason of the deactivation was the oligomerized products of ethylene, typically butenes, although other polymerization-cracking products are present. These products were re-circulated back to the reactor and accumulated on catalysts after further polymerization. It was observed in our previous studies that such reactions took place readily deep in “pseudo-liquid phase”. So, in order to suppress the formation of oligomers, the dispersion (or thickness) of heteropolyacid layer on silica was carefully controlled by changing the way of preparation, the amount of loading, etc. as well as the surface area and pore-size distribution of silica. If the layer is very thin, partial decomposition of polyanion may take place, but, if it is too thick, in addition to the decrease of the surface area, the oligomerization tends to proceed more easily in the solid bulk of heteropolyacid, namely in pseudo-liquid phase. The surface area and pore-size distribution were also very relevant to the control of the layer structure. In these studies BN-TPD (Fig. 4) was helpful to estimate the layer structure. Besides, impurities in the support such as Al and Fe caused significant oligomerization, so that they were eliminated as much as possible.

In addition to the improvements of the catalyst, the partial pressure of steam in the feed was precisely chosen and the temperature in the catalyst bed was controlled very carefully. Fig. 8 illustrates that, in a certain narrow range of partial pressure of steam, the formation of oligomerized products can be suppressed, maintaining a high yield. As a result of all these efforts, ethyl acetate the improved catalyst exhibited much longer catalyst life. The catalyst life increased to more than two years at the 1.3 times higher productivity.

The greenness of the improved process is compared with the existing processes in Table 1.

2.3. Direct synthesis of acetic acid by oxidation of ethylene [3c,7]

Acetic acid is widely used for the syntheses of a variety of chemicals and the production in the world was about 8.3 million tons in 2006 and is growing by ca. 5% every year. Existing processes utilize liquid-phase reactions: (i) carbonylation of methanol, (ii) oxidation of acetaldehyde, and (iii) oxidation of alkanes like butane. These processes have drawbacks such as corrosion, hazardous wastes and/or costly catalysts.

Showa Denko commercialized in 1997 a process of gas-phase oxidation of ethylene to acetic acid. In order to improve the performance of this process, similar techniques as described in Section 2.2 were applied by the collaboration of the same groups.

Table 1
Greenness of the new process compared with the conventional processes for the synthesis of ethyl acetate.

	New process (from ethylene)	Esterification with sulfuric acid (from ethanol)	Wacker – Tischenko
Atom efficiency	Excellent	Moderate (water)	Moderate (by-product, CO_2)
Waste water	Excellent	Fair (TOC)	Poor (TOC)
Safety	Excellent	Fair (H_2SO_4)	Moderate (acetaldehyde)
Spent catalyst	Good	Moderate (sulfates)	Poor (halogenated)

TOC: Total organic compounds.

The essential components of the catalyst were Pd, Te, and heteropolyacid ($H_4SiW_{12}O_{40}$), all being supported on silica gel. All of these components including silica are indispensable to achieve a high yield and selectivity. Pd/SiO_2 gave only CO_2, and $H_4SiW_{12}O_{40}$/SiO_2 only a small amount of ethanol. In contrast, Pd and $H_4SiW_{12}O_{40}$ supported on SiO_2 showed high activity and selectivity to acetic acid. The addition of Te to Pd/SiO_2 before impregnation of heteropolyacid further improved the activity and selectivity.

The reaction mechanism is presumed to be a Wacker-type oxidation to acetaldehyde, followed by its oxidation to acetic acid (Eq. (3)), while a route of hydration to ethanol followed by oxidation was assumed in early stage of development.

$$CH_2{=}CH_2 \rightarrow CH_3CHO \rightarrow CH_3COOH \qquad (3)$$

The state of $H_4SiW_{12}O_{40}$ supported on SiO_2 was important as in the case of ethyl acetate synthesis. The rate of formation of acetic acid increased with an increase in the loading level of $H_4SiW_{12}O_{40}$ and reached a maximum at 20–30 wt% of loading. At this loading level, $H_4SiW_{12}O_{40}$ was dispersed on SiO_2 as several layers, as indicated by BN-TPD (see Section 2.1). When the loading level increased beyond this level, the activity decreased probably because the layer becomes too thick to form large islands (low dispersion) and covering the Pd particles that are the essential component.

In addition to the control of the layer structure of heteropolyacid as in the case of ethyl acetate, the contact between Pd and heteropoly was maximized for the present reaction, as it was probable that heteropolyacid assists to maintain a high oxidation state of Pd and high dispersion of Pd. It was suggested by Kamiya et al. [7] that Te also accelerates the re-oxidation of Pd that is reduced to a lower oxidation state during the Wacker-type reaction.

As a result of these efforts, the catalyst life increased more than two times at a 50% higher space time yield. Greenness of this process is compared with the carbonylation process in Table 2.

Table 2
Comparison of greenness and economy between two processes for the synthesis of acetic acid.

	Oxidation of ethylene (present process)	Methanol carbonylation
Atom efficiency	Good	Good
Waste water	Good	Good
Chemical hazards	Good	Fair (CO)
Catalyst	Fair	Poor (halide and expensive Rh)
Feedstock	Good (flexible to ethanol)	Good (flexible to various carbon sources)
Plant cost	Moderate	High

3. Perovskite catalysts

The second example is the application of perovskite-type mixed oxides to environmental catalysts. Perovskite-type mixed oxides have been studied as oxidation catalysts over 30 years [8]. We have carried out a considerable amount of basic studies on the catalysis of perovskite-type mixed oxides taking advantage of their well-characterized solid structure of ABO_3, where stable A cations and oxide ions form a cubic closest packing in ideal case, B cations (transition metals in our study) being located in octahedral interstices surrounded by six oxide ions. We deduced five principles for the basic design of perovskite catalysts [8b,9].

1. Selection of B site transition metals.
2. Valence control of B site transition metals.
3. Combination of B1 and B2 such as Cu and Mn.
4. High surface area (thin layer on support or nanocrystallites).
5. Combination with noble metals.

The perovskite catalysts thus designed have high oxidation activity, e.g., for complete oxidation of hydrocarbons to CO_2, so that they are used as environmental catalysts. The subject described here is related to the fifth of the five principles, namely, the combination of noble metals and perovskite for automotive catalysts. Before describing the application to automotive catalyst, earlier examples of practical application of perovskite catalysts that were developed based on the principles 1–3 will be

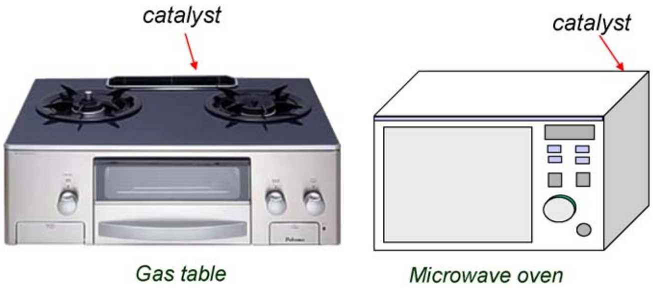

Fig. 9. Perovskite catalysts for household appliances.

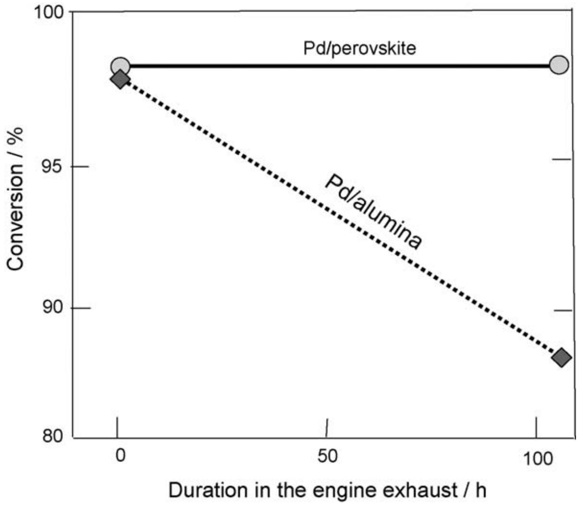

Fig. 10. Comparison of catalyst life in automotive exhausts between Pd/perovskite and Pd/alumina [11].

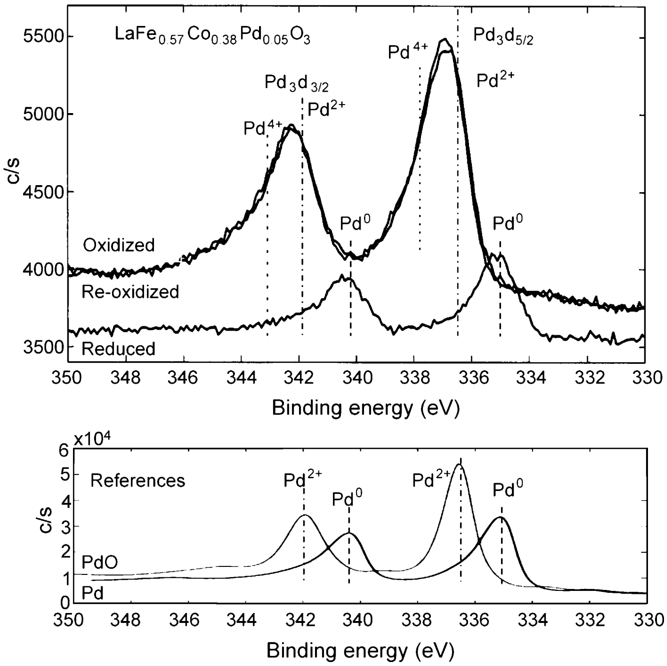

Fig. 11. XPS of oxidized and reduced Pd/perovskite catalyst (Pd3d) [10].

mentioned. They are to improve the amenity of daily life, namely, usage in cooking equipments in kitchen such as gas table and microwave oven, as shown in Fig. 9. Catalysts are perovskite powders coated on monolith-type ceramics and located on the top or back of the equipments, as indicated in Fig. 9. They eliminate or reduce smoke and smell coming out during cooking. These devices are very popular from the 1980s in Japan, and are among the earliest examples of catalytic technology applied in this area.

Next the application of Pd-loaded perovskite for automotive three-way catalyst will be described [10,11]. The idea of embedding noble metals in or on perovskite may not be very novel, but successful application in practical use and clarification of the structure were first realized by the research and development carried out by Tanaka and co-workers at Daihatsu Motor Company. The author's group contributed in the fundamental aspects. For example, it was investigated how the catalytic activity and thermal stability vary with the composition of La–Sr–Fe–Co–O perovskite and how the catalytic activity rises upon the addition of Pd [12].

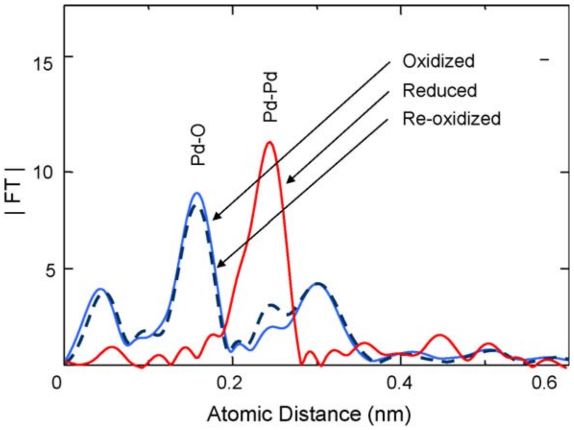

Fig. 12. EXAFS of oxidized and reduced Pd/perovskite catalyst. Radial structure function around Pd [11].

Pd/perovskite showed much higher durability and, therefore, the amount of Pd required in the fresh catalyst was very much suppressed, i.e., less than one-third of the conventional catalysts. The high durability was made possible by the reversible and rapid transformation of the state of Pd in the atmosphere of automotive emission, that is, between Pd ion (oxidized state) in the lattice of perovskite and Pd nanocrystallite (reduced metallic state) on the surface of perovskite. Under the real conditions, the emission frequently alternates between oxidizing and reducing atmosphere, and this brings about the reversible transformation of the state of Pd, that was confirmed by several physical methods, as described below.

First, much higher durability of Pd/perovskite catalyst than the ordinary Pd/alumina may be evident from the results shown in Fig. 10 [11].

Fig. 11 shows some of the XPS data. Upon reduction and re-oxidation Pd reversibly changes its oxidation state between oxidized ionic and reduced metallic states. It is notable that the oxidation state is higher than plus 2, suggesting that Pd is in the

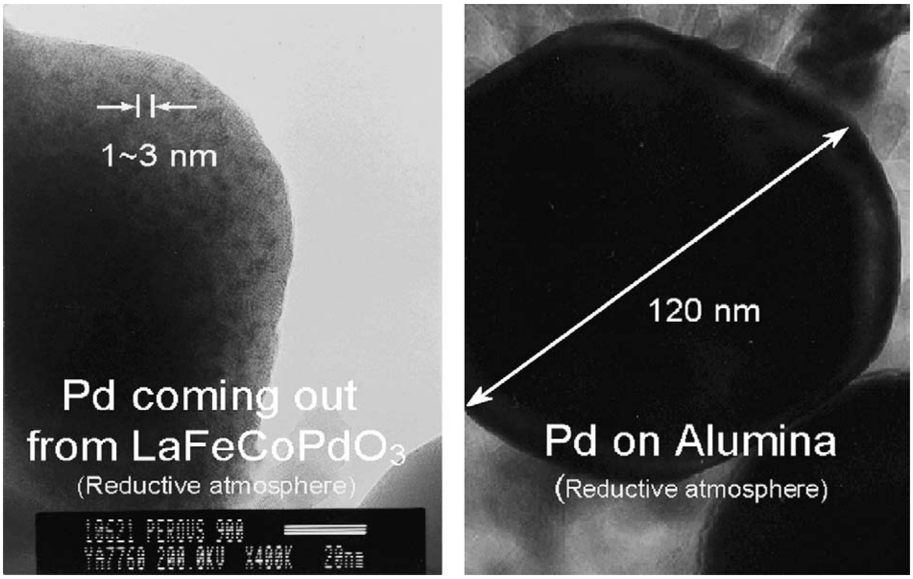

Fig. 13. TEM images of Pd/perovskite (left) and Pd/alumina (right) after duration experiments. The particle size of Pd is 1–3 nm for Pd/perovskite and 120 nm for Pd/alumina [10].

perovskite lattice, since the formal oxidation state must be plus 3 in the lattice of ABO_3 (A and O are +3 and −2, respectively).

EXAFS data given in Fig. 12 are consistent with the reversible change between the two states. It may be evident that the Pd–Pd bond is present in the reduced sample and the Pd–O bond in the oxidized sample.

So-called X-ray anomalous diffraction was applied as well, where the incident energy was swept in a short range, fixing at a certain diffraction angle of perovskite. The behavior of dip and cusp observed in the spectra shows that the change of the Pd state is connected with perovskite lattice and indicates that Pd is really present in the lattice of perovskite [10]. In situ measurement of EXAFS further demonstrated that the process is very rapid at a high temperature (873 K). That is, upon the change of atmosphere between oxidizing and reducing atmosphere, the spectrum changed rapidly and reversibly in a few seconds.

In fact, the particle size of Pd in Pd/perovskite catalyst after long duration in automotive exhaust is much smaller than that of the conventional Pd/alumina catalysts, as is obvious in TEM images shown in Fig. 13 (1–3 nm vs. 120 nm). Daihatsu group called the mechanism *self-regeneration mechanism* and the catalyst *intelligent catalyst*, as it recognizes the atmosphere by itself and changes its state automatically.

4. Summary

Two examples of green catalytic processes using supported heteropolyacid and another example of environmental catalysts utilizing a combination of Pd and perovskite are described. Both were already used in large-scale processes or in a huge number of cars. The former catalysts could be further improved in future by more precise control of the structure of supported heteropolyacids, and the concept demonstrated in the latter examples may be widely used for other applications where precious metals are indispensable catalyst components. The author believes that potential capabilities of catalysts in the sustainable society are unlimited, so that more efforts in fundamental and application studies to develop efficient practical catalysts are very much needed.

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