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Highlight Review

Environmental Catalysts for Complete Oxidation of Volatile Organic Compounds and Methane

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Abstract

Excellent oxidation catalysts, which can completely oxidize volatile organic compounds (VOCs) and methane at moderate temperatures, have been prepared. A new concept based on the design of solid electrolytes has been applied to the preparation of the catalysts. By the synergetic effect of precious metals and rare earth oxides, complete oxidation of VOCs and methane into CO_2 and steam at moderate temperatures has been realized for the present catalysts.

◆ Introduction

Examples of volatile organic compounds (VOCs) are ethylene, toluene, xylene, formaldehyde, acetaldehyde, ethyl acetate, and dichloromethane, which vaporize easily and diffuse into the atmosphere under ambient conditions. The VOCs are not only responsible for unpleasant odors in paint and printing plants, chemical factories and our living environment but also are harmful to human health and the environment and recognized to cause sick building syndrome and multiple chemical sensitivity.[1–3] To keep us and the environment away from such harmful influences, it is necessary to oxidize these VOCs into carbon dioxide and water vapor in order to suppress their release into the atmosphere.

Among the VOCs mentioned above, ethylene plays a biological role as a plant hormone that enhances ripening. It acts at trace levels throughout the life of the plant by stimulating or regulating the ripening of fruits, the blooming of flowers, and the abscission (or shedding) of leaves. In high concentrations, however, it accelerates the spoilage of fruit and vegetables. Toluene and acetaldehyde are widely used as organic solvents for paints, antiseptics, and adhesives, but they have offensive odor and cause sick building syndrome when they are vaporized into the atmosphere.

Meanwhile, methane (CH_4) is excluded from VOCs, but it is a highly potent greenhouse gas, and its greenhouse effect is about 20 times higher than that of CO_2. Therefore, it is important to keep these emissions into the atmosphere as low as possible. However, methane is probably the most difficult of all the alkanes to oxidize completely over a catalyst, because its oxidation must be carried out at much higher temperatures than other alkanes.

For the effective abatement of VOCs and methane, several methods have been proposed, such as adsorption processes,[4,5] catalytic decomposition using ozone and plasma,[6,7] photocatalytic decomposition,[8,9] and catalytic combustion.[10] Among these methods, catalytic combustion of VOCs by complete oxidation into carbon dioxide and steam is a method to oxidize VOCs on the surface of the catalysts and is an ecologically simple and clean technology to eliminate them at moderate temperatures.[10] However, it is significantly difficult to realize complete oxidation of the VOCs at moderate temperatures. Actually, reaction temperature of at least 150 °C is necessary to achieve total oxidation.[11–13] Thus, it is extremely significant to develop a novel oxidation catalyst which can realize complete combustion of VOCs at temperatures as low as possible.

In order to develop novel catalyst that can completely oxidize VOCs and methane at low temperatures, our interest has been focused on the investigation of novel materials that can supply reactive oxygen not only from the surface but also from the bulk, by employing our original concepts based on solid-state chemistry and solid-state ionics (solid electrolytes) into the catalyst design.[14] As a result, it was found that CeO_2–ZrO_2–Bi_2O_3 solid solutions exhibit much better oxygen storage and release properties than those of conventional CeO_2–ZrO_2 solid solutions.[15–17] Furthermore, we elucidated that the CeO_2–ZrO_2–Bi_2O_3 solid solutions supported on high-surface-area γ-Al_2O_3 show remarkable oxygen storage and release abilities below 100 °C, even in the absence of precious metals.[18,19]

In this highlight review, we present the construction of the novel oxidation catalysts, which can realize complete combustion of VOCs and methane into carbon dioxide and steam at moderate temperatures without production of any foul smelling and combustible by-products. These may be considered to be safe, secure, and maintenance-free environmental catalysts. The catalysts consist of a CeO_2–ZrO_2–Bi_2O_3 solid solution and ultrafine particles based on noble metals (Pt or Pd) supported on the surface, and in many cases, γ-Al_2O_3 is also employed to enhance the specific surface area of the catalysts. Ethylene,[20] toluene,[21] and acetaldehyde[22] were selected as the VOCs to be purified by the catalysts. Furthermore, the oxidation activity of methane[23] was also examined.

◆ Complete Oxidation of Ethylene below 100 °C on the Pt/CeO_2–ZrO_2–Bi_2O_3/γ-Al_2O_3 Catalyst

To begin with, the effect of the reducibility of the support was investigated by taking the ethylene oxidation activity as an example. Figure 1 shows the temperature dependencies of

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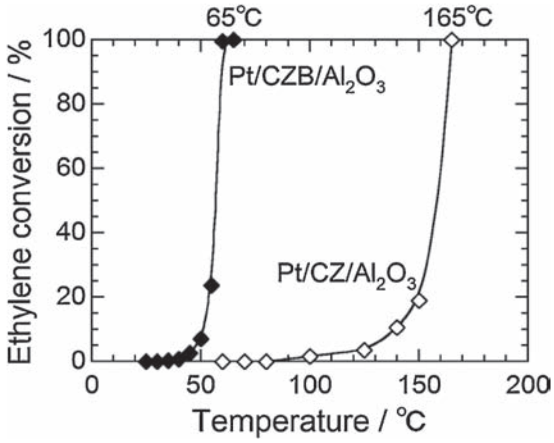

Figure 1. Temperature dependencies of ethylene combustion to CO_2 and steam on the $Pt/CZB/Al_2O_3$ and the $Pt/CZ/Al_2O_3$ catalysts (C_2H_4: 1 vol%; O_2: 4 vol%, He balance; $W/F = 0.3$ g s cm^{-3}, where W and F are the catalyst weight and the gas flow rate, respectively).

ethylene oxidation on a $Pt(3\,wt\%)/Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}(16\,wt\%)/\gamma\text{-}Al_2O_3$ catalyst (hereafter denoted as $Pt/CZB/Al_2O_3$) and a $Pt(3\,wt\%)/Ce_{0.80}Zr_{0.20}O_{2.0}(16\,wt\%)/\gamma\text{-}Al_2O_3$ ($Pt/CZ/Al_2O_3$) catalyst. The amount of platinum was optimized for the most effective ethylene oxidation,[20] and the Ce:Zr ratio in CeO_2–ZrO_2–Bi_2O_3 and CeO_2–ZrO_2 was fixed to be 80:20 to have excellent redox properties.[14,18,20] It was confirmed that only carbon dioxide (CO_2) and steam (H_2O) were produced by the complete oxidation of ethylene, and no ethylene-derived compounds were detected as by-products by gas chromatography mass spectrometry.

As evidenced by the activity data shown in Figure 1, the catalytic activity was significantly enhanced when CeO_2–ZrO_2–Bi_2O_3 was employed as the promoter rather than CeO_2–ZrO_2, because Bi_2O_3, which is a high oxide-anion conductor, was dissolved into the lattice of the CeO_2–ZrO_2 solid. The reasons for choosing Bi_2O_3 as the dopant and the basic principle of the catalyst design are discussed in detail later.

On the conventional catalysts reported before this study, the lowest temperature for complete oxidation of ethylene was 150 °C.[11] In contrast, total oxidation of ethylene on the $Pt/CZB/Al_2O_3$ catalyst was realized at a temperature as low as 65 °C,[20] which is the lowest temperature ever reported.

Complete Oxidation of Toluene on the Pt/CeO_2–ZrO_2–$Bi_2O_3/\gamma\text{-}Al_2O_3$ Catalyst

The oxidation activity of the Pt/CeO_2–ZrO_2–$Bi_2O_3/\gamma\text{-}Al_2O_3$ catalyst was evaluated to investigate whether the catalyst is also effective toward the combustion of aromatic VOCs. The catalytic activities in toluene oxidation of a $Pt(7\,wt\%)/Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}(16\,wt\%)/\gamma\text{-}Al_2O_3$ catalyst and a $Pt(7\,wt\%)/Ce_{0.80}Zr_{0.20}O_{2.0}(16\,wt\%)/\gamma\text{-}Al_2O_3$ catalyst were tested in a flow of air containing 900 ppm toluene, as depicted in Figure 2. Toluene was completely oxidized into CO_2 and H_2O, and CO and any toluene-derived compounds were not detected as by-products, as similarly observed in the oxidation of ethylene.[20]

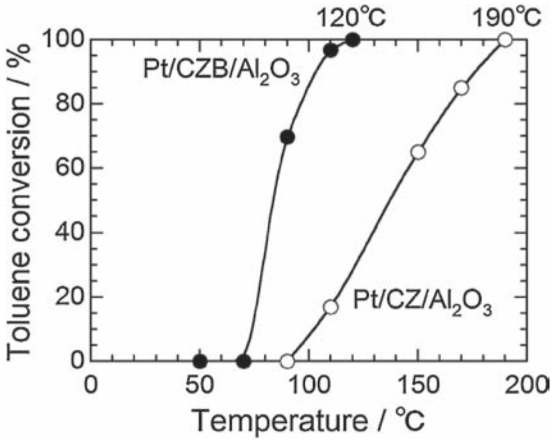

Figure 2. Temperature dependencies of toluene combustion to CO_2 and steam on the $Pt/CZB/Al_2O_3$ and the $Pt/CZ/Al_2O_3$ catalysts (C_7H_8: 900 ppm; air balance; $W/F = 0.3$ g s cm^{-3}).

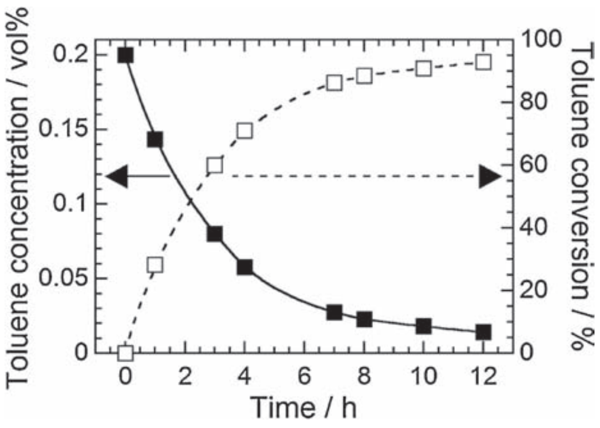

Figure 3. Simulation of the toluene conversion in a compact chamber using the $Pt/CZB/Al_2O_3$ catalyst (volume of the chamber: 1 m^3; catalyst: 0.2 g, catalyst temperature: 200 °C, initial toluene concentration: 0.2 vol%).

Also in the case of toluene, the Bi_2O_3 doping into the CeO_2–ZrO_2 lattice is significantly effective to promote the toluene oxidation. Although a reaction temperature of at least 170 °C was necessary to achieve the total oxidation of toluene in the case of the conventional catalysts,[12,24–39] complete oxidation of toluene was realized at a temperature as low as 120 °C for the present catalyst.[21]

Furthermore, a simulation of the toluene conversion in a compact chamber, in which 0.2 g of catalyst and 0.2 vol% (2000 ppm) toluene in air are introduced, was carried out using the $Pt(7\,wt\%)/Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}(16\,wt\%)/\gamma\text{-}Al_2O_3$ catalyst. The catalyst temperature was set at 200 °C, and the gas was allowed to circulate in the chamber with three air-circulating fans. The simulation result is depicted in Figure 3. The concentration of toluene decreased from 2000 ppm to 140 ppm after 12 h, where the toluene conversion reached 93%. As a result, it has become evident that the catalyst prepared in the present study shows high purification activity.

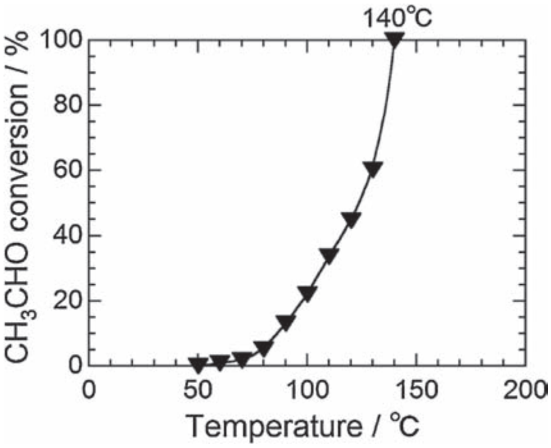

Figure 4. Temperature dependencies of acetaldehyde combustion to CO_2 and steam on the Pt/CZB catalyst (CH_3CHO: 1 vol %; air balance; $W/F = 0.36\,g\,s\,cm^{-3}$).

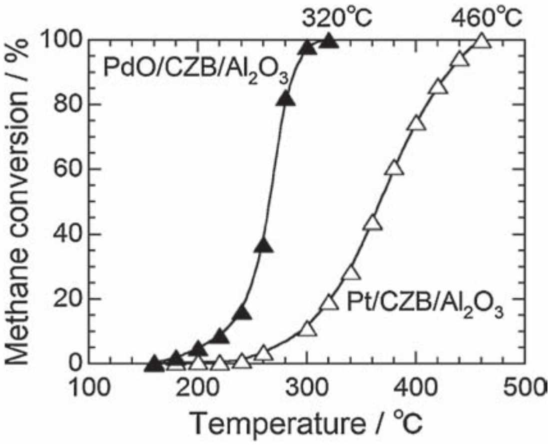

Figure 5. Temperature dependencies of methane combustion to CO_2 and steam on the PdO/CZB/Al_2O_3 and the Pt/CZB/Al_2O_3 catalysts (CH_4: 1 vol %; air balance; $W/F = 0.18$ $g\,s\,cm^{-3}$).

◆ Complete Oxidation of Acetaldehyde on the Pt/CeO_2–ZrO_2–Bi_2O_3 Catalyst

Similarly, the catalytic activity in acetaldehyde oxidation of the Pt(10 wt %)/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$ (Pt/CZB) catalyst was also evaluated in a flow of air containing 1 vol % acetaldehyde. Figure 4 shows the temperature dependencies of acetaldehyde combustion on this catalyst.[22] Also in this case, total oxidation of acetaldehyde into CO_2 and steam was confirmed by the gas chromatography analysis.

Although some combustion catalysts for acetaldehyde abatement have been reported,[13,40,41] it is significantly difficult to realize complete oxidation of acetaldehyde at moderate temperatures, and actually the catalyst has to be heated at least up to 200 °C.[13] In contrast, however, complete oxidation of acetaldehyde was realized at a temperature as low as 140 °C, which was significantly lower than that ever reported on the conventional catalysts.[22]

◆ Complete Oxidation of Methane on the Pt/CeO_2–ZrO_2–Bi_2O_3/γ-Al_2O_3 and PdO/CeO_2–ZrO_2–Bi_2O_3/γ-Al_2O_3 Catalysts

The present Pt/CeO_2–ZrO_2–Bi_2O_3/γ–Al_2O_3 catalyst shows high oxidation activity for aliphatic not only unsaturated but also saturated hydrocarbons. However, in the case of methane combustion, PdO-based catalysts exhibit higher activity for the catalytic combustion of methane than those of Pt-based catalysts.[23] This tendency is attributable to the difference in the chemical activity of oxygen adsorbed on the surface of Pt and PdO particles toward the oxidation of methane. It is difficult for oxygen molecules adsorbed on platinum from the gas phase to readily activate the almost nonpolar C–H bonds in methane, while O^{2-} ions in PdO can activate the C–H bonds easily.[42] PdO is reduced to metallic Pd, when oxygen in PdO is consumed for the methane combustion. However, the metallic Pd is reoxidized immediately to PdO by the lattice oxygen from the CeO_2–ZrO_2–Bi_2O_3 solid solution. Then, the oxygen molecules from the gas phase are adsorbed on the surface of the CeO_2–ZrO_2–Bi_2O_3 solid and are introduced into the bulk to reproduce the original promoter. Accordingly, it is necessary to supply reactive oxygen from the bulk to accomplish the complete oxidation of methane at the lowest possible temperatures.

Figure 5 depicts the temperature dependencies of methane oxidation on the PdO(12 wt %)/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$(16 wt %)/$\gamma$-$Al_2O_3$ (PdO/CZB/Al_2O_3) and the Pt(7 wt %)/$Ce_{0.64}Zr_{0.16}$-$Bi_{0.20}O_{1.90}$(16 wt %)/γ-Al_2O_3 (Pt/CZB/Al_2O_3) catalysts. The amounts of PdO and Pt were optimized to show the highest oxidation activities. As evidenced in Figure 5, the oxidation activity of PdO-supported catalyst is higher than that of Pt catalysts, and complete oxidation of methane was realized over the PdO/CZB/Al_2O_3 catalyst at a temperature as low as 320 °C,[23] which is lower than those ever reported for the conventional catalysts.[43–53] Furthermore, it was confirmed that the catalyst was stable and was not deactivated after being used for a straight week: 100% conversion of methane to CO_2 and steam was maintained even after leaving it in the gas stream at 320 °C.

◆ Mechanism of High Catalytic Activity

The catalysts described above were designed by the combination of active oxygen supplied from the CeO_2–ZrO_2–Bi_2O_3 promoter and high oxidation activity of noble metals. An oxide material that can release oxygen from the lattice at moderate temperatures was selected as the support to promote the oxidation, and noble metals were highly dispersed on the surface of the support. Consequently, we succeeded in preparing significantly active catalysts which can realize complete oxidation of VOCs and methane at lower temperatures than those reported to date.

Typical and representative materials that can supply oxygen from the bulk are CeO_2–ZrO_2 solid solutions, which have been practically applied as promoters in automotive exhaust catalysts.[54–56] However, it is difficult for the oxygen release from CeO_2–ZrO_2 solid solutions to function well below 500 °C. This oxygen release temperature is too high to completely oxidize VOCs and methane at moderate temperatures.

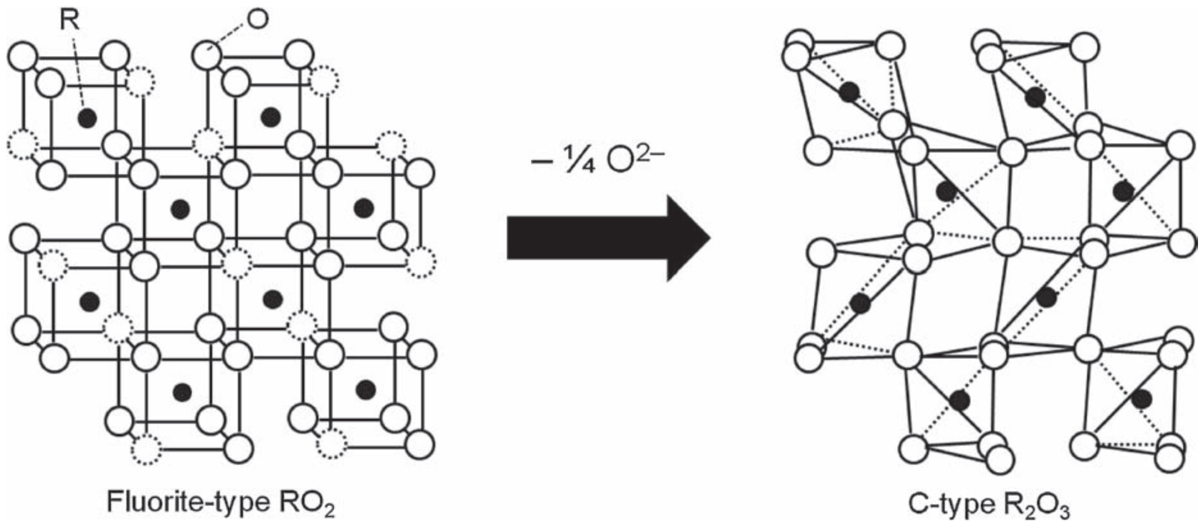

Figure 6. The relationship between the cubic fluorite oxide (RO_2; R: rare earths) and the C-type cubic bixbyite sesquioxide (R_2O_3). The solid dots indicate the rare earth ions. Removal of one-fourth of the oxygen atoms of the fluorite type oxide along nonintersecting strings in the four $\langle 111\rangle$ directions results in the formation of the C-type structure.

Therefore, we deliberated a method to accelerate the oxygen release and storage (redox) properties at a temperature as low as possible. As a result, it was found that the introduction of a small amount of bismuth oxide (Bi_2O_3) within the CeO_2–ZrO_2 lattice of the cubic fluorite structure was considerably effective to enhance the redox activity of the solid solutions.[14–19]

The reasons why we took notice of bismuth oxide and chose it as the third component are described as follows.

(1) Both cubic Bi_2O_3 and cubic Bi_2O_3–R_2O_3 (R = Y and La–Yb) solid solutions are known as excellent solid electrolytes in which only oxide anion (O^{2-}) can migrate inside the lattice.[57–61] The high oxide anion conductivities are favorable to promote the oxide anion migration inside the cubic CeO_2–ZrO_2 lattice.

(2) Bi_2O_3 is easily reduced at approximately 550 °C to release oxygen. For solid electrolytes, it is a disadvantage that Bi_2O_3 can be reduced so easily in a reducing atmosphere as to become nonfunctional immediately. However, this property is preferable to promote the oxygen release from the bulk of the oxidation catalysts at lower temperatures.

(3) Oxide anion vacancies have to be produced within the lattice to maintain charge compensation, because Bi^{3+} has lower valence (trivalent) than Ce^{4+} and Zr^{4+} (tetravalent). The vacancies also contribute to the enhancement of the oxide anion mobility.

As listed above, the crystal chemistry of inorganic materials and basic concepts of solid-state ionics (solid electrolytes) are brought into the catalyst design. In particular, the cubic Bi_2O_3 (δ-phase) exhibits extremely high oxide ion conduction, where the O^{2-} conductivity becomes almost three orders of magnitude higher than that of the low-temperature monoclinic α-phase and overtakes the conductivity of 1 M aqueous HCl solution.[14] The crystal structure of the cubic δ-phase is similar to that of cubic C-type (bixbyite-type) rare earth sesquioxide and belongs to a defect fluorite-type structure. The C-type cubic structure includes a large amount of vacant sites in the lattice in which one-fourth of the oxygen atoms in the fluorite structure are removed as illustrated in Figure 6.[62] Furthermore, application of the ready reducibility of Bi_2O_3 is a come-from-behind idea, which has been considered a disadvantage for solid electrolytes to cause electronic conduction. We took into account these advantages more preferentially in designing the oxidation catalysts for VOCs and methane and realized the novel combustion catalysts.[63]

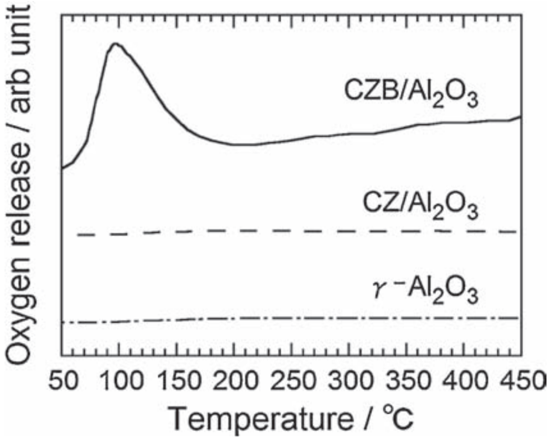

Figure 7. Temperature-programmed reduction profiles of CZB/Al_2O_3 and CZ/Al_2O_3. For reference, the reduction behavior of the γ-Al_2O_3 support is also included.

The significant positive effect of the Bi_2O_3 doping into the CeO_2–ZrO_2 lattice most glaringly appeared in the temperature-programmed reduction (TPR) profile,[18] which indicates oxygen release ability of the material. Comparisons of the TPR profiles of $Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$(20 wt %)/$\gamma$-$Al_2O_3$ (CZB/Al_2O_3), $Ce_{0.80}Zr_{0.20}O_{2.0}$(20 wt %)/$\gamma$-$Al_2O_3$ (CZ/Al_2O_3), and γ-Al_2O_3 are shown in Figure 7. There was not any noteworthy reduction peak in the profile of the conventional CZ/Al_2O_3 and γ-Al_2O_3 in the temperature range below 450 °C. In contrast, a significant reduction peak was observed at around 100 °C for CZB/Al_2O_3. This remarkable feature can be attributed to the high reducibility of Bi_2O_3 and the formation of oxide anion vacancies in the solid solution, leading to the enhancement of the oxide anion conductivity.

On the basis of the above results, the concerted combination of the excellent oxygen-release property of the CeO_2–ZrO_2–Bi_2O_3 solid solution and high oxidation activity of noble metals is the key factor for the catalysts in the present study to have significantly higher oxidation activities than those of conventional catalysts.

◆ Concluding Remarks and Future Perspectives

Novel environmental catalysts based on CeO_2–ZrO_2–Bi_2O_3 solid solutions have been prepared for complete oxidation of not only VOCs such as ethylene, toluene, and acetaldehyde but also methane. The present catalysts have been designed from unique concepts based on the design of solid electrolytes, which are usually overlooked. The high oxidation activities for VOCs and methane were successfully realized by the combination of the excellent oxygen-release property of the CeO_2–ZrO_2–Bi_2O_3 support and high oxidation activity of noble metals.

For future perspective, it is necessary to realize complete combustion of VOCs and methane at around room temperature or below for environmental purification by catalysis to be in widespread use. Although perfect ethylene combustion at 65 °C was realized in our study, further enhancement of the activity is required for practical applications. We hope that the strategy for material design based on solid-state ionics and inorganic materials chemistry will serve as the foundation for future development of novel environmental catalysts.

In recent years, rare metals have become increasingly difficult to obtain. Our catalysts utilize precious platinum and palladium in a precise amount. However, for realizing complete combustion, these noble metals are essential. What is important is to reuse and to recycle the precious metals such as Pt and Pd and to utilize the high performance for sustainable chemistry.

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