

Study of Low-temperature CO Oxidation Cycle on Precious Metal-supported CeO₂

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ABSTRACT

Low-temperature active catalysts that oxidate CO at low temperatures and use the reaction heat produced to convert HC and NOx are available as technologies to respond to the reduction of exhaust gas temperatures as a result of the achievement of increased fuel efficiency. Pd/CeO₂ catalysts, in which a palladium catalyst is supported on a cerium oxide carrier, represent one of these technologies. The mechanism of supply and resupply of active oxygen by the cerium oxide carrier was focused on and an analysis was conducted in order to increase the low-temperature activity of these catalysts. This study resulted in the determination of a mechanism of low-temperature CO oxidation able to accelerate the CO oxidation reaction from low temperatures by means of the achievement of supply of active oxygen from low temperatures through the use of highly dispersed palladium particles, and the achievement of rapid and high-volume resupply of active oxygen through the coexistence of H₂O and O₂.

1. Introduction

Demands for the reduction of emissions of CO₂, a factor in global warming, are today increasing. The achievement of increased fuel efficiency is critical to reducing CO₂ emissions, and a variety of technologies are available to respond to this need, including increase of combustion efficiency and hybridization of powerplants. It can be assumed that these technologies will result in increased automotive emissions by reducing the temperature of exhaust gases and expanding the range that is not converted by the catalyst at engine start. The development of a catalyst able to convert target emissions (carbon monoxide (CO), hydrocarbons (HC), and nitrogen oxide (NOx)) from lower temperatures than existing catalysts (a low-temperature active catalyst) can therefore be considered necessary.

Gold (Au) catalysts^{(1),(2)} and palladium-supported cerium oxide catalysts (Pd/CeO₂)⁽³⁾ that oxidize CO at low temperatures and use the reaction heat to convert HC and NOx are available as low-temperature active catalysts. However, the use of Au catalysts in automotive applications is challenging, given their low heat resistance. The temperature range at which Pd/CeO₂ catalysts oxidate CO is higher than that of Au catalysts, necessitating performance enhancements, but the catalysts are heat-resistant and can be employed as automotive catalysts. Pd/CeO₂ catalysts

were therefore focused on, and research was conducted on enhancing their low-temperature activity.

Research has recently been progressing on the characteristics of active oxygen desorbed by oxygen storage/release materials, as exemplified by cerium oxide (CeO₂)⁽⁴⁾⁻⁽⁶⁾. This research has shown that when palladium (Pd) is supported on cerium oxide (CeO₂), the substances exert a mutual interaction at the Pd/CeO₂ interface⁽⁷⁾. In addition, steam (H₂O) in exhaust gas is adsorbed at areas in which the Pd is activated, inhibiting the CO oxidation reaction⁽⁸⁾.

Oxidation reactions can be initiated from low temperatures using the active oxygen desorbed by CeO₂. In order to enhance the low-temperature activity of Pd/CeO₂, it was necessary to achieve supply of the active oxygen desorbed by the surface of the CeO₂ to the Pd at a lower temperature, and to resupply the surface of the CeO₂ with active oxygen more rapidly. In addition, it was also necessary to study the effect of H₂O, which normally reduces CO oxidation performance.

Study of the mechanism of supply and resupply of active oxygen in Pd/CeO₂ catalysts in this research showed that rather than simply being adsorbed at points of Pd activation, when it impedes the CO oxidation reaction, H₂O more generally promotes the resupply of active oxygen, and therefore accelerates the CO oxidation reaction from lower temperatures. The modification of the catalyst based

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on this result reduced the temperature at which 50% of HC, CO, and NO_x is converted (the light-off temperature) by approximately 20°C.

This report will discuss the determination of the mechanism of low-temperature oxidation of CO by means of the study of supply and resupply of active oxygen, which represented an important orienting factor in the modification of the catalyst.

2. Study of Promotion of Supply of Active Oxygen

Figure 1 shows a hypothetical mechanism scheme of low-temperature oxidation of CO by desorption of active oxygen.

As (1) in Fig. 1 shows, it is theorized that CO oxidation reactions tend not to occur at low temperatures in the palladium-supported alumina catalysts (Pd/Al₂O₃) that are widely used as automotive catalysts because they do not release active oxygen at low temperatures.

As (2) and (3) in Fig. 1 show, in the case of a Pd/CeO₂ catalyst, the Pd donates electrons to the CeO₂, promoting the desorption of active oxygen by the CeO₂ contiguous to the Pd. The Pd can therefore be supplied with active oxygen from low temperatures. It is conjectured that the supplied active oxygen and the CO adsorbed by the Pd react, promoting the oxidation of CO at low temperatures. However, when the diameter of the Pd particles is large, as shown in (2), little active oxygen is desorbed from low temperatures, and there is a minimal effect of promotion of the CO oxidation reaction at low temperatures. When the Pd particles are small in diameter (when the particles have been refined), as in the case of (3), it is theorized that because there is a significant amount of electron donation from the Pd to the CeO₂, and the amount of active oxygen that can be supplied from low temperatures also increases, there is a significant effect of promotion of the CO oxidation reaction at low temperatures.

In order to demonstrate the validity of the hypothetical mechanism scheme shown in Fig. 1, the amount of active oxygen supplied was measured using Pd/Al₂O₃ and two types of Pd/CeO₂ with particles of different sizes (Fig. 2). The diameter of the Pd particles was measured

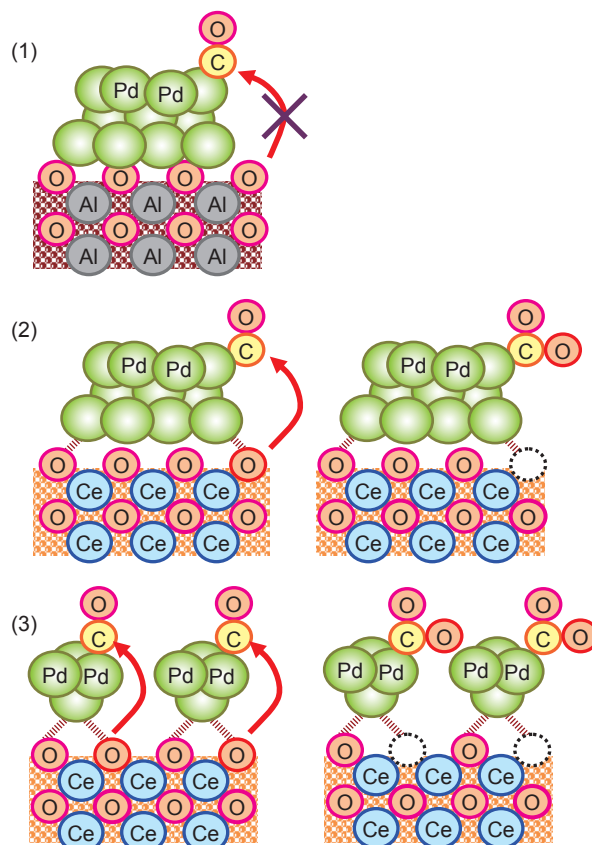
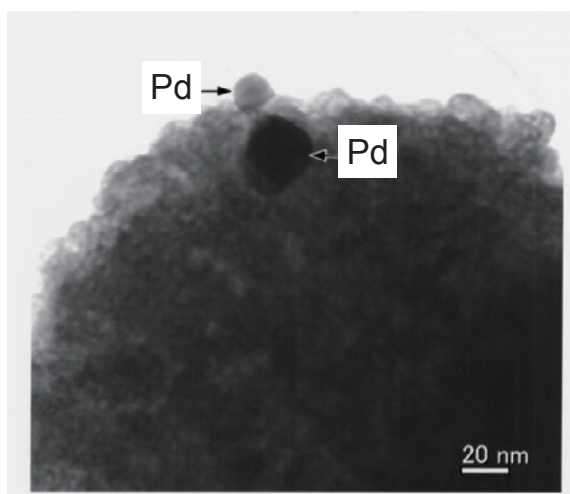
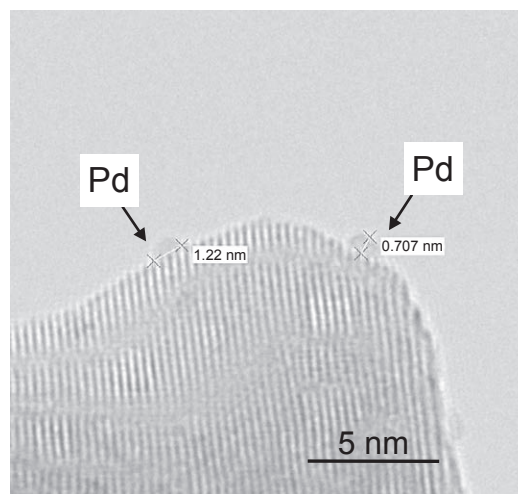


Fig. 1 Mechanism scheme of CO oxidation on (1) Pd-supported Al₂O₃, (2) Pd (large particle size)-supported CeO₂ and (3) Pd (small particle size)-supported CeO₂



(a) Pd/CeO₂ (Pd particle size: 20 nm)



(b) Pd/CeO₂ (Pd particle size: 1 nm)

Fig. 2 TEM image of Pd (1 wt%)/CeO₂

using transmission electron microscopy (TEM). The amount of active oxygen supplied was calculated from the concentration of reacted CO₂ when a CO-N₂ mixed gas was heated from room temperature to 400°C at 20°C / min using a Simulated Gas Generator & Catalyst Test System manufactured by HORIBA, Ltd. The results are shown in Fig. 3.

While the Pd/Al₂O₃ desorbed almost no active oxygen at temperatures of 200°C and below, the tests showed that the Pd/CeO₂ released active oxygen at these temperatures. In addition, the results indicated that while the Pd with a particle size of approximately 20 nm desorbed active oxygen from approximately 200°C, the Pd with a particle size of approximately 1 nm desorbed it from approximately 100°C. The CO conversion of the Pd/Al₂O₃ and the two forms of Pd/CeO₂ with differing Pd particle sizes was also studied. The results are shown in Fig. 4. In the conversion tests, a mixed gas of CO, O₂, H₂O, and N₂ was heated

from room temperature to 450°C at 20°C / min using the Simulated Gas Generator & Catalyst Test System. The gas was measured following reaction, and the CO conversion at each temperature interval was measured. The results shown in Fig. 4 indicate that the Pd/CeO₂ is able to oxidate CO from a lower temperature than the Pd/Al₂O₃. In addition, the results show that the CO light-off temperature of the CeO₂ supported on Pd particles of approximately 1 nm in diameter was approximately 64°C lower than that of the CeO₂ supported on Pd particles of approximately 20 nm in diameter.

The results discussed above indicate that active oxygen supplied from the surface of the carrier is an important factor in the oxidation of CO at low temperatures. In addition, the highly dispersed Pd particles enhance the mutual interaction of the Pd and Ce, and this boosts CO oxidation performance by promoting the supply of active oxygen from low temperatures.

3. Study of Resupply of Active Oxygen

When active oxygen is supplied, oxygen disappears from the surface of the CeO₂ (oxygen defects), and if oxygen is not resupplied, the active oxygen necessary for the CO oxidation reaction cannot be supplied. Resupply by oxygen within the CeO₂ (bulk oxygen) and resupply from the components of the gas formed during the reaction can be considered as mechanisms of resupply of oxygen-to-oxygen defects.

First, resupply of oxygen defects by means of bulk oxygen was examined. Figure 5 compares results for the CO conversion of the Pd/CeO₂ catalyst and temperatures for bulk oxygen desorption by CeO₂. In the CO conversion

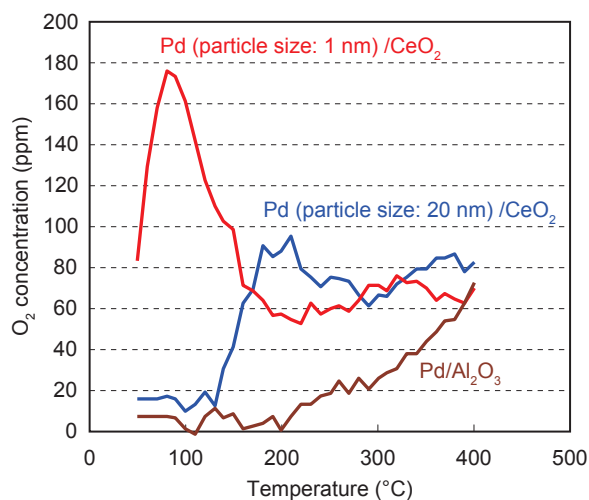


Fig. 3 O₂ release temperature of different Pd particle size-supported CeO₂ and Pd/Al₂O₃

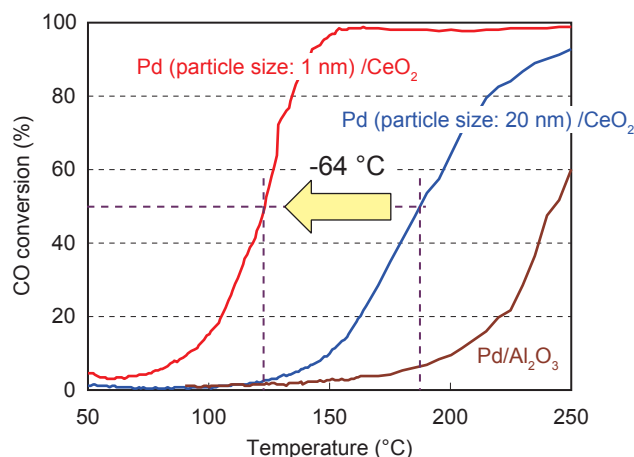


Fig. 4 Conversion for CO oxidation over different Pd particle size-supported CeO₂ and Pd/Al₂O₃

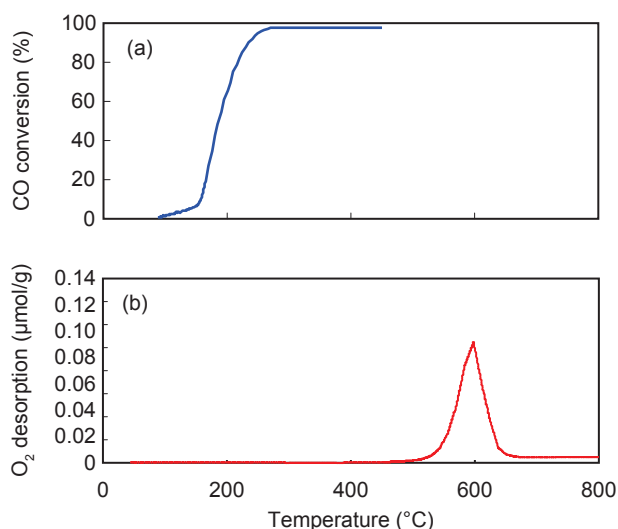


Fig. 5 Concern of O₂ desorption from CeO₂ and CO light-off temperature
(a) CO light-off (catalyst: 1 wt% Pd/CeO₂ fresh)
(b) O₂-TPD (catalyst: CeO₂)

tests, a mixed gas of CO, O₂, H₂O, and N₂ was heated from 50°C to 450°C at 20°C / min using the Horiba Simulated Gas Generator & Catalyst Test System. The gas was measured following reaction, and the CO conversion at each temperature interval was measured. The amount of bulk oxygen desorbed at each temperature was measured using O₂ temperature programmed desorption (O₂-TPD). The results showed a significant difference in temperature, with a CO light-off temperature of approximately 200°C and a temperature for desorption of bulk oxygen of approximately 600°C. Given this, it was unlikely that CeO₂ bulk oxygen was contributing to the resupply of active oxygen, and it was therefore conjectured that resupply from the components of the gas formed during the reaction was the mechanism of resupply.

The gas formed in the CO conversion test contained carbon monoxide (CO), oxygen (O₂), water (H₂O), and nitrogen (N₂). Of these, O₂ and H₂O are the components able to resupply oxygen.

Figure 6 shows the results of tests conducted to determine the effect of CO and O₂, CO and H₂O, and CO, O₂, and H₂O mixed gases (N₂ balance) on CO conversion. Oxidation of CO occurs in the presence of both O₂ and H₂O, but the catalyst light-off temperature in the case of O₂ is approximately 190°C lower than that of H₂O. In addition, the results show that H₂O has an effect in promoting

the CO conversion, with the light-off temperature being approximately 30°C lower when O₂ and H₂O are present together than when O₂ is present in isolation.

Given this, it was conjectured that active oxygen would be resupplied by the coexistence of O₂ and H₂O.

Figure 7 shows the theoretical mechanism scheme of this resupply. First, in the case of resupply by H₂O ((a) in

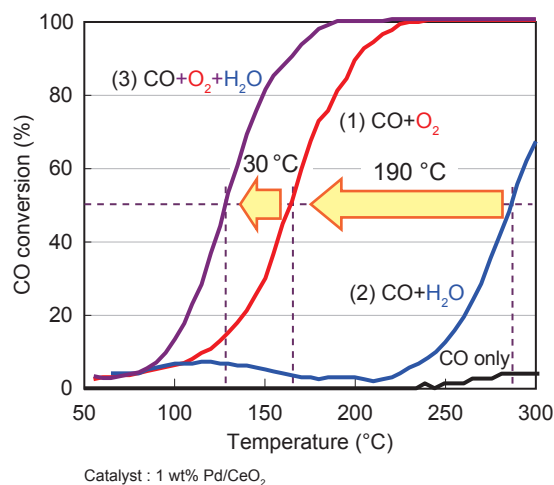


Fig. 6 Effect of CO conversion with (1) O₂, (2) H₂O and (3) H₂O+O₂ addition

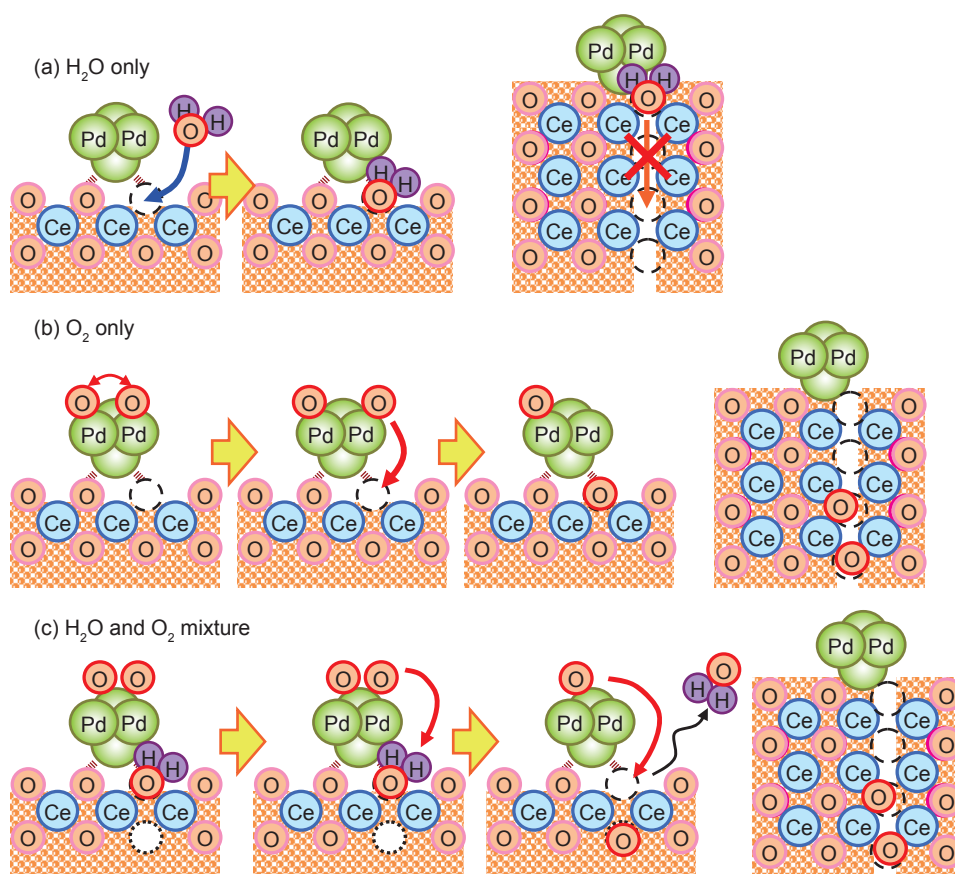


Fig. 7 Mechanism scheme of O₂ supply on CeO₂ with addition of (a) H₂O only, (b) O₂ only and (c) H₂O and O₂ mixture

the figure), resupply is rapid because H₂O is able to directly resupply oxygen defects in the surface. However, because the H₂O molecules are larger in size than the oxygen defects (steric hindrance), the molecules are unable to penetrate to the interior, and only resupply the surface. In the case of resupply by O₂ ((b) in the figure), because resupply commences after adsorption and disaggregation of the O₂ by the Pd, the speed of resupply is slow. However, oxygen atoms are small, and they are able to penetrate into the interior.

Considering the combined effect of H₂O and O₂ in terms of these mechanisms, it can be conjectured that the H₂ formed during resupply of oxygen defects by H₂O ((c) in the figure) rapidly react with O₂, and oxygen atoms are resupplied in the interior. In addition, the oxygen atoms not used in the reaction are resupplied. It is theorized that in this way, the H₂ produced as a result of the coexistence of H₂O and O₂ promotes the resupply of oxygen-to-oxygen defects.

In order to demonstrate the validity of this hypothetical mechanism, different gases (O₂, H₂O, and H₂O+O₂) were released with CeO₂ in a reduced state, and the performance of each gas in resupplying oxygen was measured. The amount of UV-visible light absorbed at 150°C was measured using ultraviolet-visible spectroscopy⁽⁹⁾⁻⁽¹¹⁾ to measure oxygen resupply performance. The results are shown in Fig. 8. The upper section of the vertical axis shows the reduced state, with the substance becoming more oxidized (increasing resupply of oxygen) with increasing distance down the axis.

The measurement results indicated the following:

- (1) H₂O displays a higher speed of resupply of oxygen defects than O₂.
- (2) H₂O produces a lower amount of resupply of oxygen defects than O₂ in isolation.
- (3) The coexistence of H₂O and O₂ results in more rapid resupply of oxygen defects than O₂ in isolation, and an

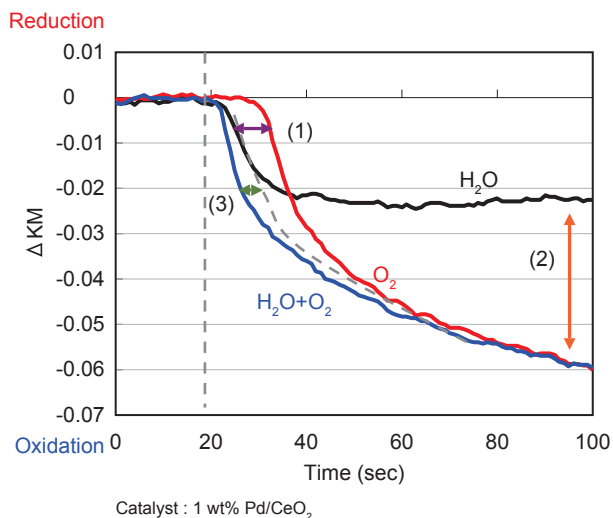


Fig. 8 UV-visible spectra of added (1) H₂O, (2) O₂ and (3) H₂O+O₂ at 423 K

equivalent amount of resupply as O₂ in isolation.

Given that, based on items (1) to (3), the effect of the coexistence of H₂O and O₂ promotes resupply of oxygen defects, it was clear that CeO₂ was taking in active oxygen from H₂O and O₂, components of the gas formed during the reaction.

Next, the contribution of the promotion of resupply of oxygen defects by the coexistence of H₂O and O₂ to the CO oxidation cycle was studied. In these tests, H₂ was added separately to H₂O, and the effect on CO conversion was examined. The results are shown in Fig. 9. The CO light-off temperature is lower in the cases of CO+O₂+H₂ and CO+O₂+H₂O than in the case of CO+O₂. H₂ promotes the oxidation of CO from low temperatures by reacting with the O₂ on the Pd, and promoting resupply of the excess O. The amount of resupply of oxygen defects is low when H₂ exists in isolation, but when H₂O forms H₂, the oxygen in the H₂O resupplies oxygen defects, and the H₂ dissociates the oxygen on the Pd, promoting oxidation of CO. Because of this, the CO light-off temperature is approximately 8% lower in the case of CO+O₂+H₂O than CO+O₂+H₂.

Figure 10 shows the mechanism scheme of low-temperature oxidation of CO, reflecting the effects of promotion of supply of active oxygen and of resupply of active oxygen, as determined in the present project.

The highly dispersed Pd particles on the CeO₂ helped results in active oxygen being supplied from approximately 100°C, and this highly dispersed Pd particles therefore promotes the commencement of the CO oxidation cycle shown as (1), (2), (3a), and (4a) in the figure (the CO cycle due to O₂ in isolation) from low temperatures.

Next, the fact that the speed of resupply of active oxygen is greatest and a high amount of resupply can be achieved in the case of coexistence of H₂O and O₂ was verified, and the CO oxidation cycle shown as (1), (2), (3b), (4b), (5b), and (6b) in the figure (the CO oxidation cycle

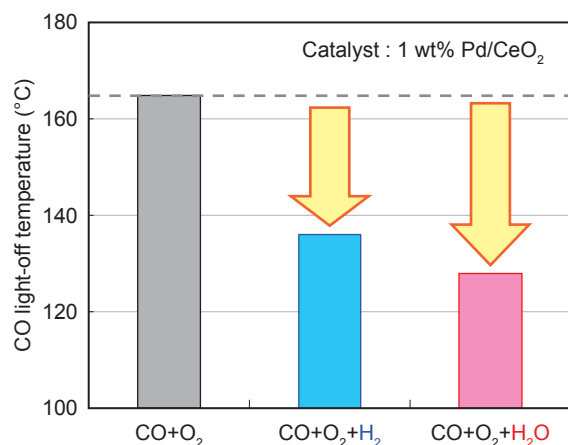


Fig. 9 Effect of added H₂ and H₂O on CO light-off temperature

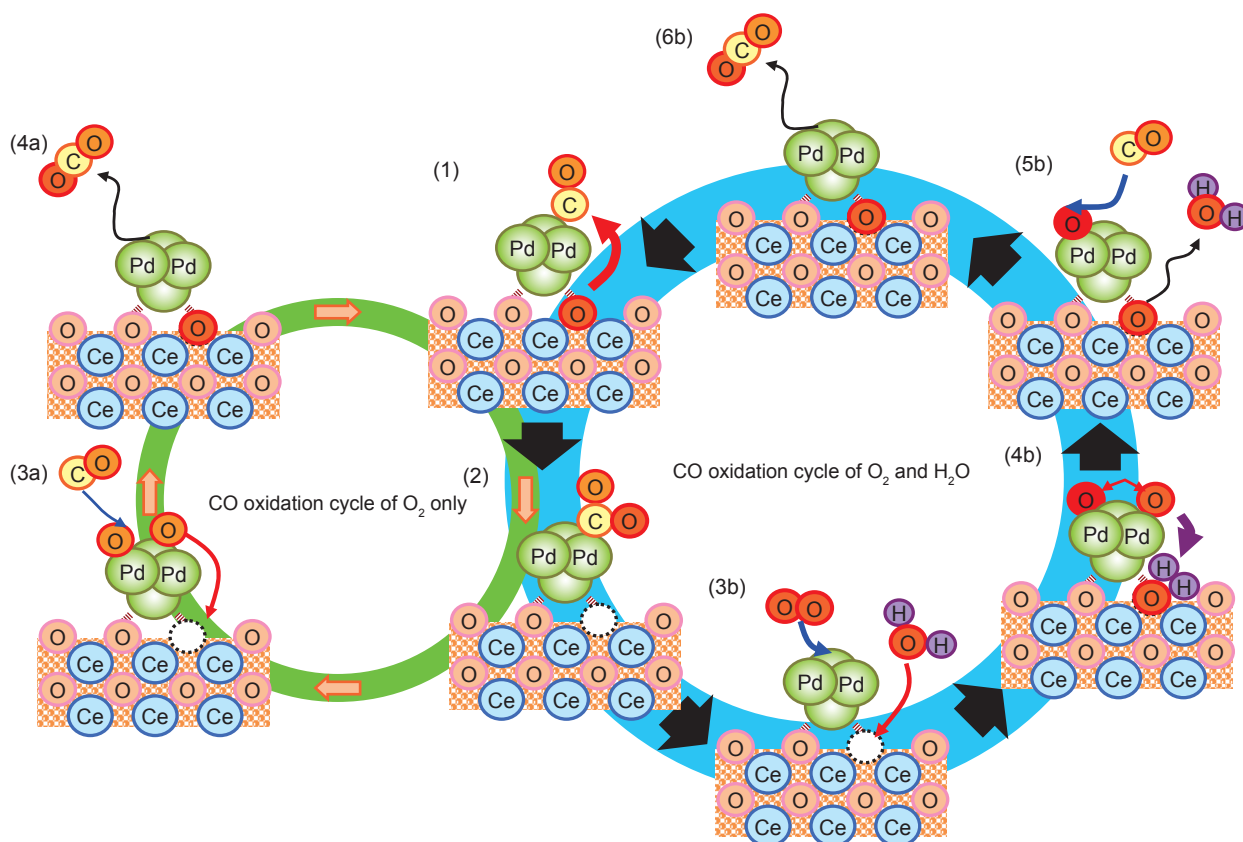


Fig. 10 Mechanism scheme of low temperature CO oxidation

due to H_2O and O_2) was identified. The results indicated that the CO oxidation cycle resulting from the presence of O_2 is supplemented by the CO oxidation cycle resulting from the presence of H_2O and O_2 , accelerating the CO oxidation reaction at low temperatures.

4. Conclusions

The project discussed here indicated that combining a CO oxidation cycle in which the resupply of active oxygen is promoted and resupply occurs in high quantities due to the coexistence of H_2O and O_2 , and a CO oxidation cycle in which the supply of active oxygen is promoted by the highly dispersed Pd particles, accelerated the CO oxidation reaction at low temperatures. Focusing on the promotion of resupply of active oxygen through the coexistence of H_2O and O_2 , knowledge obtained in the present project, it was possible to identify methods of reformation of low-temperature CO oxidation catalysts through consideration of additive elements to CeO_2 and other factors.

References

- (1) Haruta, M.: Low-temperature Combustion Catalysts -Mainly for CO Oxidation-, Journal of the Japan Petroleum Institute, Vol. 37, No. 5, p. 480-491 (1994)
- (2) Date, M., Haruta, M.: Support Effects on the Catalysis of Gold Nanoparticles and Their Applications, Catalysts & Catalysis, Vol. 47, No. 1, p. 8-13 (2005)
- (3) P 05-285387
- (4) Takami, A., Takita, Y.: Syokubaiseinou ni Oyobosu Kinzokuhukugousankabutsu no Tantaikouka ni kansuru Kenkyu III, Annual Report of Research and Development Center Oita University, No. 13, p. 55-56 (2008) (in Japanese)
- (5) Fan, J., Weng, D., Wu, X., Wu, X., Ran, R.: Modification of CeO_2 - ZrO_2 mixed oxides by coprecipitated/impregnated Sr: Effect on the microstructure and oxygen storage capacity, J. Catal., Vol. 258, No. 1, p. 177-186 (2008)
- (6) Fujita, T., Osumi, K., Nakamura, K., Tashiro, Y.: Pt/ CeO_2 kei Sankasyokubai no Sanso Kyuuhausyutsukinou, 100th CATSJ Meeting Abstracts, p. 268 (2007) (in Japanese)
- (7) Hinokuma, S., Fujii, M., Okamoto, M., Ikegami, K., Machida, M.: Pd/ CeO_2 no Netsusyori niyoru CO Sankasyokubaikassei no Koujou, 105th CATSJ Meeting Abstracts, p. 31 (2010) (in Japanese)
- (8) P3952314
- (9) Binet, C., Badri, A., Lavalley, J.: A Spectroscopic Characterization of the Reduction of Ceria from Electronic Transitions of Intrinsic Point Defects, J.

Phys. Chem., Vol. 98 (25), p. 6392-9398 (1994)

- (10) Oda, T., Shimizu, K., Satsuma, A.: Ag/CeO₂ Syokubai niyoru CO Sankahannou ni okeru Kasseiseigyoinshi, 102nd CATSJ Meeting Abstracts, p. 181 (2008) (in Japanese)
- (11) Oda, T., Shimizu, K., Satsuma, A.: CO Sankayou Koutainetsusei Rh/CeO₂ Syokubai, 104th CATSJ Meeting Abstracts, p. 455 (2009) (in Japanese)

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