Rh Supported on LaPO₄/SiO₂ Nanocomposites as Thermally Stable Catalysts for TWC Applications

Haris Puspito Buwono¹ · Taishi Eidome¹ · Saki Minami¹ · Satoshi Hinokuma^{1,2} · Yuki Nagao³ · Yunosuke Nakahara³ · Masato Machida^{1,2}

Received: 19 May 2015 / Revised: 10 July 2015 / Accepted: 13 July 2015 / Published online: 7 August 2015
© Springer SIP, AG 2015

Abstract Hydrothermally synthesized LaPO₄/SiO₂ nanocomposites were investigated as thermally stable support materials for Rh catalysts. The nanocomposites were composed of macroporous SiO₂ and highly dispersed columnar LaPO₄ crystallites of approximately 20 nm in thickness and 100 nm in length, the surface of which anchored Rh nanoparticles via Rh–O–P interfacial bonding. The microstructure was useful to prevent agglomeration and sintering of LaPO₄ during high-temperature thermal aging under both oxidizing and reducing atmospheres. The Rh catalyst supported on the LaPO₄/SiO₂ composite exhibited higher catalytic activities for simulated NO–CO–C₃H₆–O₂ reactions over a wide Rh loading range (0.01–0.4 wt%), compared to those of Rh catalysts supported on the individual components (LaPO₄ and SiO₂), and on ZrO₂, which is widely used as a support for Rh in commercial three-way catalysts. Enhanced catalytic activities for elementary CO–O₂, CO–H₂O, and CO–NO reactions were achieved while maintaining the activity toward C₃H₆ as an advanced feature of phosphate supports.

Electronic supplementary material The online version of this article (doi:10.1007/s40825-015-0024-9) contains supplementary material, which is available to authorized users.

✉ Masato Machida
machida@kumamoto-u.ac.jp

¹ Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Chuo, Kumamoto 860-8555, Japan

² Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, 1-30 Goryo-Ohara, Nishikyo, Kyoto 615-8245, Japan

³ Catalysts Strategic Division, Engineered Materials Sector, Mitsui Mining & Smelting Co., Ltd., 1013-1 Ageosho, Ageo, Saitama 362-0025, Japan

Keywords Rhodium · Phosphate · Three-way catalyst · Nanocomposite · Metal–support interaction

1 Introduction

Currently, more than 80 % of the Rh demand is for the three-way catalyst (TWC) because of its high efficiency to convert NO to N₂ in the autoexhaust [1–5]. Rh is among the scarcest of precious metals so the development of catalysts with decreased Rh content is needed. Toward this aim, many attempts have involved the use of metal–support interactions to suppress sintering [6–18]. In particular, the interactions at the interface between Rh oxide and oxide support materials have attracted considerable attention. Tanabe et al. reported recently that Nd₂O₃-doped ZrO₂ efficiently stabilizes Rh nanoparticles through Rh–O–Nd interfacial bonding [15]. Similar anchoring mechanisms have been reported for Pt and Pd supported on CeO₂ [10–13, 17, 19], which are based on electrostatic interactions at the metal/oxide support interface under an oxidizing atmosphere. However, it should be pointed out that Rh oxide is difficult to reduce to active metallic Rh, as the metal–support bonding is strong. This trend leads to a trade-off between thermal stability and catalytic activity, which should be taken into consideration when designing active and thermostable Rh catalysts with a minimum Rh loading.

In a series of our preceding papers [20–26], another type of the Rh anchoring mechanism on metal phosphates, which stabilize Rh nanoparticles via Rh–O–P interfacial bonding, was reported. The Rh–O–P bonding is preserved under both an oxidizing atmosphere and a reducing atmosphere, whereas conventional metal oxide supports form the interfacial bonding only under oxidizing conditions [22]. In addition, the Rh–O–P linkage enables smooth reduction of Rh oxide to metallic Rh and improves

resistance to reoxidation [23, 24]. Because the metallic Rh is more active than Rh oxide for most elementary reactions in the TWC [27–29], this resistance is beneficial for practical applications. The catalytic activity is also affected by the acidic nature of metal phosphates; hydrocarbons such as C_3H_6 are efficiently converted to aldehyde intermediates, which are highly reactive to NO and O_2 adsorbed on Rh [23]. This feature is most obvious for the Rh/ZrP₂O₇ catalyst, which demonstrated pronounced NO_x reduction efficiency under slightly lean conditions [24]. Conversely, the Rh–O–P linkage provides electron-deficient Rh due to electron-withdrawing effects from the acidic phosphate group [23]. This favors the decreasing back-donation from the Rh *d*-orbitals to the π^* molecular orbitals of chemisorbed CO and/or NO, which has a negative impact on the catalytic activity for CO–O₂, CO–H₂O, and CO–NO reactions. To overcome this negative effect and to promote the desirable characteristics, the acidity of phosphate materials was controlled using metals with a higher basicity [25]. Consequently, LaPO₄ was found to be the best material, which achieved both the high thermal stability and catalytic activity for TWC elementary reactions.

Toward further enhancement of the catalytic performance, a novel preparative approach for higher specific surface areas of LaPO₄ is necessary. In this study, LaPO₄/metal oxide nanocomposite materials were prepared as supports for Rh catalysts expecting a beneficial effect on the thermal stability compared with LaPO₄ alone. Because Rh/LaPO₄/SiO₂ nanocomposites exhibited the highest catalytic activity for simulated NO–CO–C₃H₆–O₂ reactions, the detailed catalytic performance was investigated as functions of Rh loading and thermal aging temperature. The local structure and metal–support interaction of supported Rh catalysts were characterized by transmission electron microscope (TEM), extended X-ray absorption fine structure (EXAFS), and chemisorption technique.

2 Experimental

2.1 Catalyst Preparation

Lanthanum phosphate (LaPO₄) was prepared from the corresponding metal nitrates (Wako Pure Chemicals) and H₃PO₄ (Wako Pure Chemicals Ind. Ltd., 85 %) [25]. A H₃PO₄ solution (0.05 mol) in deionized water (50 mL) was added dropwise to the nitrate solutions (0.05 mol) of deionized water (50 mL) with vigorous stirring. After dropwise addition of aqueous ammonia (25 %) to adjust the pH to 9, the resulting slurry was hydrothermally treated at 200 °C for 18 h. As-formed white gel was recovered by centrifugation, washed several times with deionized water, and dried in air at

100 °C. The solid product was calcined in air at 900 °C for 5 h. Nanocomposite supports consisting of LaPO₄ and metal oxides (γ -Al₂O₃, SiO₂, or ZrO₂) were also prepared by the hydrothermal synthesis and post-calcination in the same way. The metal oxides for this purpose were supplied by the Catalysis Society of Japan (JRC-ALO-8, JRC-SIO-9A, and JRC-ZRO-3) and were added to the slurry before the hydrothermal synthesis. The LaPO₄ content in each composite solid was in a range of 5–40 mol%. Supported Rh catalysts (0.01–0.4 wt% as Rh metal) were prepared by impregnation of an aqueous solution of Rh(NO₃)₃ followed by air-drying at 100 °C and air calcination at 600 °C for 3 h. As-prepared catalysts were heated to 900–1100 °C for 25 h in flowing 10 % H₂O/air in order to evaluate their thermal stability under an oxidizing atmosphere (hydrothermal aging). The catalysts thus aged at 900 °C were subsequently treated at 200–800 °C for 5 h in 20 % H₂/He in order to evaluate their thermal stability under a reducing atmosphere.

2.2 Characterization

Powder X-ray diffraction analysis was performed using monochromatic Cu K α radiation (30 kV, 20 mA, Multiflex, Rigaku), and the Rh content was determined by energy-dispersive X-ray fluorescence (EDXL300, Rigaku). The FE-TEM micrographs were acquired using an FEI TECNAI F20 transmission electron microscope operating at 200 kV. Brunauer–Emmett–Teller (BET) surface area (S_{BET}) was calculated using N₂ adsorption isotherms obtained at –196 °C (Belsorp-mini, Bel Japan). The Rh metal dispersion was determined by pulsed CO chemisorption at 50 °C (Belcat, Bel Japan) after a reduction treatment at 400 °C in 20 % H₂/He. The metal dispersion is expressed in terms of the molar ratio of chemisorbed CO per loaded Rh (CO/Rh).

The local structure around Rh was investigated by EXAFS. The Rh loading for this purpose was increased to 2 wt% to ensure the spectral quality. The Rh K-edge EXAFS was recorded on an NW10A station at the Photon Factory Advanced Ring, High Energy Accelerator Research Organization (KEK) using a Si(311) double-crystal monochromator. The spectra were recorded at room temperature in a transmission mode by monitoring incident and transmitted X-rays with 17- and 31-cm-long ionization chambers filled with Ar and Kr, respectively. XAFS data were processed using the REX 2000 program (Rigaku). EXAFS oscillations were extracted by the fitting of a cubic spline function through the post edge region. The k^3 -weighted EXAFS oscillation in the 30- to 138-nm^{–1} region was Fourier transformed. For the curve-fitting analysis, phase shifts and backscattering amplitude functions of the Rh–Rh and Rh–O–Rh shells were extracted from the EXAFS data obtained for Rh foil and Rh₂O₃. The curve-

fitting analysis of the Rh–O–P and Rh–O–Si shells was performed using theoretical parameters.

2.3 Catalyst Performance Testing

Catalytic reactions were performed in a flow reactor at an atmospheric pressure. The as-prepared or thermally aged catalyst (50 mg, 20 mesh) was fixed in a quartz tube (4-mm inside diameter) using quartz wool at both ends of the catalyst bed. The temperature dependence of the catalytic activity was evaluated by heating the catalyst bed ($W=0.05$ g) from room temperature to 600 °C at a constant rate of 10 °C min⁻¹ while supplying a simulated exhaust gas mixture containing NO (0.050 %), CO (0.510 %), C₃H₆ (0.039 %), O₂ (0.400 %), and He (balance) at $F=100$ cm³ min⁻¹ ($W/F=5.0 \times 10^{-4}$ g min cm⁻³). This gas composition corresponds to the stoichiometric air-to-fuel ratio ($A/F=14.6$). The gas feed and the catalyst bed were heated using an infrared image furnace equipped with two ellipsoidal reflectors (RHL-E25P, Ulvac Riko). The effluent gas was analyzed using a Pfeiffer GSD30101 mass spectrometer and Horiba VA3000 Non-dispersive infrared (NDIR) gas analyzers. Catalytic activities for eight elementary reactions were also evaluated in a similar manner [see Table S1 in Electronic supplementary material (ESM)].

3 Results and Discussion

3.1 Rh Supported on Nanocomposite LaPO₄ Support Materials

To demonstrate a negligible influence of mass transfer and heat transfer contributions in our catalytic microreactor, the change in the conversion was measured as a function of gas flow rate (and thus the W/F value). When the conversion was below 50 %, the reaction rate was proportional to the W/F value, suggesting that the reaction was controlled by chemical kinetics. A Madon–Boudart criterion was applied to evaluate the effect of internal mass transport using one of our reference catalysts (see Fig. 3) with 0.4 and 0.2 wt% Rh loadings, which showed similar metal dispersions. The similarity of the TOF at each of two different temperatures indicates that the measured rates were not influenced by mass transport limitations. When a simulated stoichiometric NO–CO–C₃H₆–O₂ reaction was performed in a light-off mode, the conversion increased very steeply to 100 % within a narrow temperature range (see Fig. S1 in ESM). In such a situation, it is difficult to compare the reaction rate at the same temperature under kinetically limited conditions. Therefore, the activity is simply expressed in terms of the light-off temperature (T_{50}) at which the conversion of NO_x, CO, and C₃H₆ reached 50 %. The T_{50} value is a reasonable parameter to compare the relative activity of the different catalysts. Table 1 summarizes the S_{BET} ,

CO/Rh, and T_{50} values for each catalyst before and after the hydrothermal aging at 900 °C for 25 h in 10 % H₂O/air. The hydrothermal aging of Rh/LaPO₄ decreased the metal dispersion (CO/Rh) from 22 to 3.7 % and thus increased the T_{50} values. Because S_{BET} of the catalyst decreased from 44.5 to 33.3 m² g⁻¹ during the hydrothermal aging, sintering of supports is a plausible deactivation mechanism. To improve the thermal stability of Rh/LaPO₄, microstructural modification of the support material was investigated. Three composite materials containing 20 mol% LaPO₄ and 80 mol% γ -Al₂O₃ ($S_{\text{BET}}=150$ m² g⁻¹), SiO₂ (310 m² g⁻¹), or ZrO₂ (38 m² g⁻¹), were prepared hydrothermally. The S_{BET} values of all these composites were lower than expected because of oxide particles growth during the hydrothermal synthesis, while improved CO/Rh values greater than 5 % were obtained after the hydrothermal aging. The as-prepared Rh catalysts using these composite supports exhibited T_{50} values comparable to those for Rh/LaPO₄. After the hydrothermal aging, however, only the SiO₂ composite could improve the activity, while the other composites with Al₂O₃ and ZrO₂ exhibited more significant deactivation than LaPO₄ alone.

The LaPO₄/SiO₂ composites with different mixing ratios (5, 10, 20, 30, and 40 mol% LaPO₄) were studied. Figure 1 plots S_{BET} , CO/Rh, and T_{50} as a function of the content of LaPO₄ for the catalysts thermally aged at 900 °C. As can be seen in Table 1 and the catalytic light-off curves (see Fig. S1 in ESM), the light-off of NO, CO, and C₃H₆ occurred at similar temperatures. The catalytic activity can therefore be expressed in terms of the T_{50} for NO. The S_{BET} was nearly constant at approximately 40 m² g⁻¹, while the CO/Rh value gave rise to the maximum at 20 mol% LaPO₄, at which point the lowest T_{50} was achieved. To elucidate this behavior, the line-broadening analysis of XRD data (see Fig. S2 in ESM for details) was performed to determine the LaPO₄ crystallite size of these composites. Because the calculated size for 20 mol% LaPO₄ (20 nm) was smaller than that of LaPO₄ alone (24 nm), the SiO₂ composite was effective in suppressing the grain growth of LaPO₄ and thus Rh nanoparticles supported on LaPO₄.

Figure 2 shows the TEM photographs of Rh/LaPO₄/SiO₂ before and after the hydrothermal aging. The as-prepared catalyst was composed of columnar LaPO₄ crystallites of approximately 20 nm in thickness and 100 nm in length, which were dispersed in the macroporous SiO₂ matrix with an amorphous morphology. After the hydrothermal aging at 900 °C, similar microstructure could be preserved and no significant growth of particles was observed. The sintering of support particles will be initiated by neck growth at around particle boundaries present in powder aggregates, and the rate of sintering should be determined by mass transport in the solid phase [30]. Therefore, dispersing LaPO₄ crystallites within macroporous SiO₂ matrix should be a promising approach to avoid direct contact between LaPO₄ crystallites and thus suppress

Table 1 Surface area (S_{BET}), metal dispersion (CO/Rh), and catalytic activity (T_{50}) of 0.4 wt% Rh supported on various supports

Support	Thermal aging ^a	S_{BET}^b ($\text{m}^2 \text{g}^{-1}$)	CO/Rh ^c (%)	T_{50}^d ($^{\circ}\text{C}$)		
				NO	CO	C_3H_6
LaPO ₄	–	44.5	22	260	248	287
	900 $^{\circ}\text{C}$, 25 h	33.3	3.7	327	317	345
LaPO ₄ /Al ₂ O ₃ ^e	–	30.4	60	258	245	267
	900 $^{\circ}\text{C}$, 25 h	26.8	6.8	387	378	412
LaPO ₄ /ZrO ₂ ^e	–	18.1	39	255	241	282
	900 $^{\circ}\text{C}$, 25 h	14.6	5.4	336	322	357
LaPO ₄ /SiO ₂ ^e	–	49.6	20	245	238	256
	900 $^{\circ}\text{C}$, 25 h	39.6	5.6	297	287	313
SiO ₂	–	310	38	263	248	261
	900 $^{\circ}\text{C}$, 25 h	154	5.3	352	348	362

^a Hydrothermal aging in 10 % H₂O/air^b BET surface area of supported Rh catalysts^c Metal dispersion expressed in terms of molar ratio of adsorbed CO and Rh loaded^d Reaction temperature at which the conversion of each gas reached 50 %^e 20 mol% LaPO₄

sintering. As shown in Table 1, SiO₂ alone could also retain CO/Rh as high as 5 % after the hydrothermal aging at 900 $^{\circ}\text{C}$, because of the highest S_{BET} value (154 $\text{m}^2 \text{g}^{-1}$) among the catalysts studied in this study. Nevertheless, the T_{50} values for Rh/SiO₂ were much higher than those for Rh/LaPO₄/SiO₂, suggesting that

improved dispersion of LaPO₄ contributed significantly to the thermal stabilization of Rh.

3.2 Catalytic Properties of Rh/LaPO₄/SiO₂

Further studies were focused on the Rh/LaPO₄/SiO₂ catalyst to evaluate its catalytic performance, and compare it with that of Rh/LaPO₄ and Rh/SiO₂. Here, Rh/ZrO₂ was used as another reference catalyst, because ZrO₂ is widely used as a support for Rh in the commercial TWC [15]. The T_{50} values (NO) for the catalysts thermally aged at 900 $^{\circ}\text{C}$ are plotted as function of Rh loading in Fig. 3. Two oxide-supported catalysts, Rh/SiO₂ and Rh/ZrO₂, exhibited steep increases of T_{50} values as the loading decreased below 0.2 wt%, resulting in a significant activity drop, which is a common feature of Rh catalysts supported on oxides as was pointed out previously [20, 25]. By contrast, LaPO₄ and LaPO₄/SiO₂ composite could reduce the Rh loading to as low as 0.05 wt% without significant increase of T_{50} , which is the most prominent feature of metal phosphates as support materials for Rh catalysts in contrast to the oxide supports [20, 22, 25]. Among metal phosphates, LaPO₄ particularly preserved the lowest T_{50} value in a range of 0.05–0.4 wt% Rh loading [25]. A further improvement could be achieved by the LaPO₄/SiO₂ composite, which was entirely different from Rh/SiO₂.

Figure 4 plots the CO/Rh value as a function of Rh loading for LaPO₄/SiO₂ and ZrO₂ after the hydrothermal aging at 900 $^{\circ}\text{C}$. These supports showed contrasting behaviors; the value tends to increase with decreasing Rh loading for LaPO₄/SiO₂, which is in complete contrast to ZrO₂. Decreasing dispersion at lower Rh loadings for Rh/ZrO₂ may be

Fig. 1 BET surface area (S_{BET}), Rh metal dispersion (CO/Rh) and light-off temperature (T_{50} for NO) of 0.4 wt% Rh catalysts supported on composites with different LaPO₄ content after hydrothermal aging at 900 $^{\circ}\text{C}$

Fig. 2 TEM images of (a) as-prepared and (b) thermally aged (900 °C for 25 h in 10 % H₂O/air) Rh/LaPO₄/SiO₂ (20 mol% LaPO₄)

associated with encapsulation of a part of the Rh oxide due to interactions at the RhO_x–ZrO₂ interface during the hydrothermal aging, as this phenomenon prevents the reduction of Rh oxide to metallic Rh or blocks the access of CO molecules. Contrary, Rh nanoparticles can be stabilized on the surface of LaPO₄ via Rh–O–P interfacial bonding as in the case for Rh/AlPO₄ and Rh/ZrP₂O₇ [22–25], which seems to be useful for higher dispersion of smaller amounts of Rh. This is in accordance with the retention of the higher catalytic activity at lower Rh loadings as shown in Fig. 3.

Figure 5 plots the T_{50} values for NO in the NO–CO–C₃H₆–O₂ reaction after the hydrothermal aging in 10 % H₂O/air at elevated temperatures. Although Rh/LaPO₄ and Rh/LaPO₄/SiO₂ showed similar dependences on temperatures up to 900 °C, further increase of aging temperature led to a steeper rise of T_{50} and thus a more pronounced deactivation for Rh/LaPO₄ compared to Rh/LaPO₄/SiO₂. The enhanced thermal stability was also obvious when compared to Rh/SiO₂, which

exhibited the largest deactivation at 900 °C because SiO₂ is well-known as one of the most weakly interacting support materials for Rh [31]. The catalytic activity was also evaluated after the hydrothermal aging at 900 °C in 10 % H₂O/air and subsequent reduction treatment in 20 % H₂/He at elevated temperatures to evaluate thermal stability under a reducing atmosphere (Fig. 6). The reduction treatment at 200 °C significantly lowered the T_{50} value, because metallic Rh was formed which is more active than Rh oxide (Rh₂O₃) for NO_x reduction. On the contrary, the T_{50} increased with further elevation of reducing temperatures because of the sintering of metallic Rh. Again, the resulting deactivation was much more significant for Rh/SiO₂ compared to that of LaPO₄ and Rh/LaPO₄/SiO₂, because of weak interactions between metallic Rh and SiO₂. Consistent with that, the metal dispersion (CO/Rh) for Rh/SiO₂ decreased significantly from 4.0 % (reduction at 400 °C) to 1.3 % (800 °C), suggesting considerable sintering of Rh on SiO₂. It is also implied that the formation of Rh silicide during the reduction pretreatment of Rh/SiO₂ at high temperatures (>500 °C) may influence the catalytic activity [32, 33]. In contrast, the Rh/LaPO₄/SiO₂ catalyst achieved the highest activity after aging over a wide temperature range under both oxidizing and reducing atmospheres. The efficient

Fig. 3 Catalytic activity (T_{50} for NO) versus Rh loading for different supported catalysts after hydrothermal aging at 900 °C for 25 h in 10 % H₂O/air

Fig. 4 Rh metal dispersion (CO/Rh) versus Rh loading for Rh/LaPO₄/SiO₂ and Rh/ZrO₂ catalysts after hydrothermal aging at 900 °C for 25 h in 10 % H₂O/air

Fig. 5 Catalytic activity (T_{50} for NO) of supported Rh catalysts (0.4 wt% Rh loading) after hydrothermal aging at each temperature for 25 h in 10 % H_2O/air

thermal stabilization requires Rh particles that are mainly located on the surface of $LaPO_4$ but not on the surface of SiO_2 .

3.3 Interaction between Rh and Support

Figure 7 compares the Fourier transforms of Rh K-edge EXAFS for $Rh/LaPO_4/SiO_2$ with those for $Rh/LaPO_4$, Rh/SiO_2 , and Rh_2O_3 . Because these data are shown without phase shift corrections, the observed peaks are shifted to shorter values with respect to the true atomic distances listed in Table 2. All of these samples showed an intense

Fig. 6 Catalytic activity (T_{50} for NO) of supported Rh catalysts (0.4 wt% Rh loading) after hydrothermal aging at 900 °C for 25 h in 10 % H_2O/air and subsequent reduction at each temperature for 5 h in 20 % H_2/He

Fig. 7 Fourier-transformed Rh K-edge EXAFS for as-prepared $Rh/LaPO_4$, $Rh/LaPO_4/SiO_2$, Rh/SiO_2 , and Rh_2O_3

peak at approximately 2.0 $\text{\AA}$, assignable to an Rh–O shell of Rh oxide. However, their second shell peaks were different from those of Rh_2O_3 , suggesting interactions at the metal–support interface. As reported previously [25], $Rh/LaPO_4$ showed the second shell peaks containing a contribution from the Rh–O–P interfacial bonding. The similar Rh–O–P shell was observed for $Rh/LaPO_4/SiO_2$, although the coordination numbers (CN) was smaller (0.64) than that of $Rh/LaPO_4$ (1.1). Unlike these samples containing $LaPO_4$, Rh/SiO_2 exhibited another peak component assignable to Rh–O–Si, which formed at the interface between Rh oxide and SiO_2 . The outstanding thermal stability of $Rh/LaPO_4/SiO_2$ is closely associated with the Rh anchoring via Rh–O–P interfacial bonding as in Rh catalysts supported on $LaPO_4$, $AlPO_4$, and ZrP_2O_7 in our previous studies [22–25].

3.4 Activity Distribution for TWC Elementary Reactions

A variety of elementary reactions are involved in TWC, and the catalytic activity distribution for each reaction provides important information. Figure 8 plots the T_{50} values for the eight elementary reactions over Rh catalysts supported on metal phosphates and reference oxides. As reported previously [23, 25], the activity distribution is strongly dependent on the basicity of the metal species on the phosphate supports. Compared to Rh/ZrO_2 , $Rh/AlPO_4$ with a very low basicity was less active for the $CO-O_2$, $CO-H_2O$, and $C_3H_6-H_2O$ reactions, while its activities for the $C_3H_6-O_2$ and $NO-C_3H_6-O_2$ reactions were higher. This trend is closely associated with the Lewis acidity of $AlPO_4$ and a resulting electron withdrawing effect, which leads to electron deficient Rh species and thus decreased back-donation from Rh d -orbitals to the

Table 2 The fitting results obtained from Rh K-edge EXAFS analysis

Catalyst	Shell	CN ^a (± 0.2)	$r/\text{\AA}^b$ (± 0.03)	$\sigma^2/10^{-2} \text{\AA}^2$ (± 0.02)
Rh/LaPO ₄	Rh–O	4.0	2.01	0.45
	Rh–O–P	1.1	3.10	0.36
	Rh–O–Rh	0.60	2.97	0.22
	Rh–O–Rh	0.73	3.51	0.22
	Rh–O–Rh	0.53	3.76	0.37
Rh/LaPO ₄ /SiO ₂	Rh–O	4.1	2.03	0.45
	Rh–O–P	0.64	3.04	0.036
	Rh–O–Rh	0.83	2.99	0.22
	Rh–O–Rh	0.59	3.48	0.22
	Rh–O–Rh	2.0	3.73	0.37
Rh/SiO ₂	Rh–O	4.0	2.04	0.13
	Rh–O–Rh	0.55	2.99	0.21
	Rh–O–Si	1.9	3.17	0.23
	Rh–O–Rh	1.0	3.51	0.64

Interval of k -space to r -space of FT is 3.0–13.8 $\text{\AA}^{-1}$ ^a Coordination number^b Atomic distance^c Debye–Waller factor

antibonding π^* orbitals of CO and NO [23]. Conversely, Rh/LaPO₄ showed much higher activities for CO–H₂O, CO–O₂, NO–CO, and C₃H₆–H₂O reactions in accordance with the higher basicity [25]. The similar activity distribution could be observed for the Rh supported on LaPO₄/SiO₂ nanocomposite. Another noteworthy feature of phosphate supports was the higher activities for C₃H₆ (NO–C₃H₆–O₂ and C₃H₆–O₂) than those of Rh/ZrO₂. This trend

is a common feature of phosphate supports and is correlated to the oxidative adsorption of C₃H₆ as aldehyde species on the phosphate surface, which are highly reactive toward O₂ as well as NO [23–25]. The activities of the Rh catalysts supported on LaPO₄ and LaPO₄/SiO₂ for these reactions were comparable. Although Rh/SiO₂ also exhibited the similar activity distribution, the Rh loading dependence of activity (Fig. 3), the thermal behavior under reducing atmosphere (Fig. 6), and the EXAFS results (Fig. 7) suggest Rh anchored on LaPO₄ plays a key role in the high catalytic performance for these elementary reactions.

4 Conclusion

LaPO₄/metal oxide nanocomposites were prepared as support materials of Rh catalysts for the TWC applications. Among SiO₂, Al₂O₃, and ZrO₂, SiO₂ afforded a thermally stable nanocomposite, which achieved the highest metal dispersion and catalytic activity for a simulated NO–CO–C₃H₆–O₂ reaction after the hydrothermal aging. In the LaPO₄/SiO₂ nanocomposite, columnar crystallites of LaPO₄ provides a Rh anchoring effect via Rh–O–P bonding were highly dispersed in the macroporous SiO₂ matrix. It is suggested that this microstructure decrease the direct contact between the LaPO₄ crystallites and thus their sintering. Consequently, the Rh/LaPO₄/SiO₂ catalysts exhibited the higher thermal stability under both oxidizing and reducing atmosphere, compared to that of Rh catalysts supported on LaPO₄ and SiO₂ alone, and this could mostly reduce the threshold Rh loading without loss of catalytic activity.

Fig. 8 Catalytic activity (T_{50}) for various TWC elementary reactions. T_{50} values for underlined gases are plotted

Acknowledgments This study was supported by Elements Science and Technology Project from the Ministry of Education, Culture, Sports, Science and Technology (MEXT). A part of this study was performed under a management of “Elements Strategy Initiative for Catalysts & Batteries” (ESICB) supported by MEXT. XAFS experiments were performed on the NW10A of Photon Factory, High Energy Accelerator Research Organization (KEK) (Proposal No. 2009G574). Authors thank Dr. Keita Ikeue (Kumamoto University) for his help on the XAFS analysis.

References

- Heck, R.M., Farrauto, R.J., Gulati, S.T.: Catalytic air pollution control: commercial technology. Wiley, New York (1995)
- Shelef, M.: Nitric oxide: surface reactions and removal from auto exhaust. *Catal. Rev. Sci. Eng.* **11**, 1–40 (1975)
- Taylor, K.C.: Nitric oxide catalysis in automotive exhaust systems. *Catal. Rev. Sci. Eng.* **35**, 457–481 (1993)
- Gandhi, H.S., Graham, G.W., McCabe, R.W.: Automotive exhaust catalysis. *J. Catal.* **216**, 433–442 (2003)
- Shelef, M., Graham, G.W.: Why rhodium in automotive three-way catalysts? *Catal. Rev. Sci. Eng.* **36**, 433–457 (1994)
- Nishihata, Y., Mizuki, J., Akao, T., Tanaka, H., Uenishi, M., Kimura, M., Okamoto, T., Hamada, N.: Self-regeneration of a Pd-perovskite catalyst for automotive emissions Control. *Nature* **418**, 164–167 (2002)
- Tanaka, H., Taniguchi, M., Uenishi, M., Kajita, N., Tan, I., Nishihata, Y., Mizuki, J.I., Narita, K., Kimura, M., Kaneko, K.: Self-regenerating Rh- and Pt-based perovskite catalysts for automotive-emissions control. *Angew. Chem. Int. Ed.* **45**, 5998–6002 (2006)
- Tanaka, H., Uenishi, M., Taniguchi, M., Tan, I., Narita, K., Kimura, M., Kaneko, K., Nishihata, Y., Mizuki, J.I.: The intelligent catalyst having the self-regenerative function of Pd, Rh and Pt for automotive emissions control. *Catal. Today* **117**, 321–328 (2006)
- Nagai, Y., Hirabayashi, T., Dohmae, K., Takagi, N., Minami, T., Shinjoh, H., Matsumoto, S.: Sintering inhibition mechanism of platinum supported on ceria-based oxide and Pt-oxide-support interaction. *J. Catal.* **242**, 103–109 (2006)
- Nagai, Y., Dohmae, K., Ikeda, Y., Takagi, N., Tanabe, T., Hara, N., Guiler, G., Pascarelli, S., Newton, M.A., Kuno, O., Jiang, H., Shinjoh, H., Matsumoto, S.: In situ redispersion of platinum autoexhaust catalysts: an on-line approach to increasing catalyst lifetimes. *Angew. Chem. Int. Ed.* **47**, 9303–9306 (2008)
- Tanabe, T., Nagai, Y., Dohmae, K., Sobukawa, H., Shinjoh, H.: Sintering and redispersion behavior of Pt on Pt/MgO. *J. Catal.* **257**, 117–124 (2008)
- Hatanaka, M., Takahashi, N., Takahashi, N., Tanabe, T., Nagai, Y., Suda, A., Shinjoh, H.: Reversible changes in the Pt oxidation state and nanostructure on a ceria-based supported Pt. *J. Catal.* **266**, 182–190 (2009)
- Nagai, Y., Dohmae, K., Teramura, K., Tanaka, T., Guiler, G., Kato, K., Nomura, M., Shinjoh, H., Matsumoto, S.: Dynamic in situ observation of automotive catalysts for emission control using X-ray absorption fine structure. *Catal. Today* **145**, 279–287 (2009)
- Newton, M.A.: Dynamic adsorbate/reaction induced structural change of supported metal nanoparticles: heterogeneous catalysis and beyond. *Chem. Soc. Rev.* **37**, 2644–2657 (2008)
- Tanabe, T., Morikawa, A., Hatanaka, M., Takahashi, N., Nagai, Y., Sato, A., Kuno, O., Suzuki, H., Shinjoh, H.: The interaction between supported Rh- and Nd_2O_3 -riched surface layer on ZrO_2 for Rh sintering suppression. *Catal. Today* **184**, 219–226 (2012)
- Kwak, J.H., Hu, J., Mei, D., Yi, C.W., Kim, D.H., Peden, C.H.F., Allard, L.F., Szanyi, J.: Coordinatively unsaturated Al^{3+} centers as binding sites for active catalyst phases of platinum on $\gamma\text{-Al}_2\text{O}_3$. *Science* **325**, 1670–1673 (2009)
- Hinokuma, S., Fujii, H., Okamoto, M., Ikeue, K., Machida, M.: Metallic Pd nanoparticles formed by Pd–O–Ce interaction: a reason for sintering-induced activation for CO oxidation. *Chem. Mater.* **22**, 6183–6190 (2010)
- Hinokuma, S., Fujii, H., Katsuhara, Y., Ikeue, K., Machida, M.: Effect of thermal ageing on the structure and catalytic activity of Pd/CeO₂ prepared using arc-plasma process. *Catal. Sci. Technol.* **4**, 2990–2996 (2014)
- Nagai, Y., Hirabayashi, T., Dohmae, K., Takagi, N., Minami, T., Shinjoh, H., Matsumoto, S.: Sintering inhibition mechanism of platinum supported on ceria-based oxide and Pt-oxide-support interaction. *J. Catal.* **242**, 103–109 (2006)
- Machida, M., Murakami, K., Hinokuma, S., Uemura, K., Ikeue, K., Matsuda, M., Chai, M., Nakahara, Y., Sato, T.: AlPO_4 as a support capable of minimizing threshold loading of Rh in automotive catalysts. *Chem. Mater.* **21**, 1796–1798 (2009)
- Ikeue, K., Murakami, K., Hinokuma, S., Uemura, K., Zhang, D., Machida, M.: Thermostable Rh catalysts supported on metal phosphates: effect of aging on catalytic activity for NO–CO–C₃H₆–O₂ reactions. *Bull. Chem. Soc. Jpn.* **83**, 291–297 (2010)
- Machida, M., Minami, S., Ikeue, K., Hinokuma, S., Nagao, Y., Sato, T., Nakahara, Y.: Rhodium nanoparticle anchoring on AlPO_4 for efficient catalyst sintering suppression. *Chem. Mater.* **26**, 5799–5805 (2014)
- Machida, M., Minami, S., Yoshida, H., Hinokuma, S., Nagao, Y., Sato, T., Nakahara, Y.: Unusual redox behavior of Rh/ AlPO_4 and its impacts on three-way catalysis. *J. Phys. Chem. C* **119**, 373–380 (2015)
- Nagao, Y., Nakahara, Y., Sato, T., Iwakura, H., Takeshita, S., Minami, S., Yoshida, H., Machida, M.: Rh/ZrP₂O₇ as an efficient automotive catalysts for NO_x reduction under slightly lean conditions. *ACS Catal.* **5**, 1986–1994 (2015)
- Machida, M., Eidome, T., Minami, S., Buwono, H.P., Hinokuma, S., Nagao, Y., Nakahara, Y.: Tuning the electron density of Rh supported on metal phosphates for three-way catalysis. *J. Phys. Chem. C* **119**, 11653–11661 (2015)
- Matsui, M., Machida, M., Sakaki, S.: Characterization of AlPO_4 (110) surface in adsorption of Rh dimer and its comparison with $\gamma\text{-Al}_2\text{O}_3$ (100) surface: theoretical study. *J. Phys. Chem. C* **119**, in press (2015)
- Haneda, M., Houshito, O., Takagi, H., Shinoda, K., Nakahara, Y., Hiroe, K., Fujitani, T., Hamada, H.: Catalytic performance of aged Rh/CeO₂–ZrO₂ for NO–C₃H₆–O₂ reaction under a stoichiometric condition. *Top. Catal.* **52**, 1868–1872 (2009)
- Dohmae, K., Nagai, Y., Tanabe, T., Suzuki, A., Inada, Y., Nomura, M.: Real-time XAFS analysis of Rh/alumina catalyst. *Surf. Interface Anal.* **40**, 1751–1754 (2008)
- Zimowska, M., Wagner, J.B., Dziedzic, J., Camra, J., Borzęcka-Prokop, B., Najbar, M.: Some aspects of metal-support strong interactions in Rh/ Al_2O_3 catalyst under oxidising and reducing conditions. *Chem. Phys. Lett.* **417**, 137–142 (2006)
- Pask, J.A., Hoge, C.E.: Thermodynamic aspects of solid state sintering. In: Kuczynski, G.C. (ed.) *Sintering and catalyst*, pp. 229–238. Plenum Press, New York (1975)
- Zhang, Z.L., Tsiopourari, V.A., Efstathiou, A.M., Verykios, X.E.: Reforming of methane with carbon dioxide to synthesis gas over supported rhodium catalysts: I. effects of support and metal crystallite size on reaction activity and deactivation characteristics. *J. Catal.* **158**, 51–63 (1996)
- Labich, S., Kohl, A., Taglauer, E., Knözinger, H.: Silicide formation by high-temperature reaction of Rh with model SiO_2 films. *J. Chem. Phys.* **109**, 2052–2055 (1998)
- Sadi, F., Duprez, D., Gérard, F., Rossignol, S., Miloudi, A.: Morphological and structural changes in reducing and steam atmospheres of SiO_2 -supported Rh catalysts. *Catal. Lett.* **44**, 221–228 (1997)