FULL PAPER

Hydrothermal synthesis and catalytic activity of Pt–Rh/CeO₂/Al₂O₃ three-way catalysts for automotive exhaust gasHiroki YAMASHITA^{1,2,†}, Takaaki OGAMI² and Kiyoshi KANAMURA¹¹Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1–1 Minami-Ohsawa, Hachioji, Tokyo 192–0397, Japan²Central Research Laboratory, Taiheiyo Cement Corporation, 2–4–2 Osaku, Sakura, Chiba 285–8655, Japan

Pt–Rh/CeO₂/Al₂O₃ was successfully synthesized by the hydrothermal method, and its chemical and physical properties as well as its catalytic activity were evaluated. Pt–Rh/CeO₂/Al₂O₃ was also synthesized by the conventional impregnation method for purpose of comparison. Pt–Rh/CeO₂/Al₂O₃ synthesized by the hydrothermal method comprised hollow CeO₂ nanorods coated with nanoparticle arrays that served as selective supports for Pt and Rh on CeO₂ surfaces. Although the lights-off temperatures of NO and C₃H₆ were similar for Pt–Rh/CeO₂/Al₂O₃ catalysts synthesized by the two methods, moreover, Pt–Rh/CeO₂/Al₂O₃ synthesized by the hydrothermal method exhibited a lower lights-off CO temperature than that synthesized by the impregnation method. Pt–Rh/CeO₂/Al₂O₃ synthesized by the hydrothermal method also exhibited better catalytic activity, which was attributed to its better dispersion of Pt and Rh than that synthesized by the impregnation method.

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1. Introduction

Catalytic converters, typically comprising a cordierite (2MgO·2Al₂O₃·5SiO₂) monolith coated with a three-way catalyst (TWC), have been widely used to remove pollutants such as carbon monoxide (CO), nitrogen oxides (NO_x), and hydrocarbons (HC) from automotive exhaust gas.^{1,2)} The pollutants are converted to harmless water (H₂O), carbon dioxide (CO₂), and nitrogen (N₂) by the TWC.^{1–10)} A TWC usually comprises Al₂O₃ as a support, CeO₂ or CeO₂–ZrO₂ as an oxygen storage material, and precious metals (Pt, Pd, and/or Rh) as active components.^{1–10)} Precious metals are essential components of TWCs. However, it is well known that precious metals are extremely expensive due to their limited availability.¹¹⁾ Therefore it is desirable to reduce the content of precious metals in TWCs at the same time, however, TWCs are required to have high thermal stability to suppress deactivation at high temperatures of in excess 1000°C,^{5,12–14)} because the temperature of automotive exhaust gas ranges from 200 to 1000°C depending on load conditions such as idling or acceleration.^{15,16)}

Considerable research has been performed on synthetic methods for enhancing catalytic activity, including the lights-off temperature and thermal stability of TWCs at

over 1000°C.^{17–22)} The precursor species of precious metals used in the synthesis of TWCs is one important factor that can improve the catalytic activity. Lin et al.¹⁷⁾ reported that a Pd/Ce_{0.67}Zr_{0.33}O₂–Al₂O₃ catalyst prepared using H₂PdCl₄ as the Pd precursor exhibited higher catalytic activity for HC and NO conversions than that using Pd(NO₃)₂ or Pd(NH₃)₄(NO₃)₂ due to its smaller PdO_x particle size, indicating better dispersion of PdO_x. Vedyagin et al.¹⁸⁾ reported that an alloyed Pd–Rh/Al₂O₃ catalyst exhibited higher catalytic activity for CO oxidation than mechanically mixed Pd/Al₂O₃ and Rh/Al₂O₃ due to suppression of sintering and stability with respect to reduction. Chen et al.¹⁹⁾ reported that Pd/CeO₂–ZrO₂–La₂O₃–Al₂O₃ synthesized by a double-solvent method exhibited higher catalytic activity than that synthesized by the conventional impregnation method due to the Pt species' better dispersion and superior reduction properties.

The morphologies of oxygen storage materials (CeO₂ or CeO₂–ZrO₂) also affect the catalytic activity of TWCs. Kim et al.²⁰⁾ reported that a CeO₂–ZrO₂-supported Rh catalyst prepared by a continuous supercritical hydrothermal method exhibited higher catalytic activity for reduction of NO by CO and higher thermal stability than that prepared by a co-precipitation method due to its coarser agglomerates of CeO₂–ZrO₂ nanoparticles. Lan et al.²¹⁾ reported that sintering of a CeO₂–ZrO₂ support for a Pd catalyst suppressed catalytic activity due to a mixed-phase composition prepared by a modified co-precipitation

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method. Wang et al.²²⁾ reported that a $\text{CeO}_2\text{-ZrO}_2/\text{Al}_2\text{O}_3$ support for a Pd catalyst synthesized by supercritical drying and micro-emulsion methods exhibited better catalytic activity than those synthesized by the co-precipitation and sol-gel methods due to its better redox properties, smaller crystallite sizes, and larger Brunauer, Emmett, and Teller (BET) surface areas.

Among all of the aforementioned synthetic methods, the hydrothermal method is the most useful for the synthesis of TWCs, because it can obtain homogeneous and well-dispersed nanoparticles.²³⁾ Recently, several researchers have reported hydrothermal synthesis of TWC-related materials such as precious-metal nanoparticles, CeO_2 , precious metal/ CeO_2 , and precious metal/carbon species.²⁴⁾⁻³¹⁾

Herein, we report a novel synthesis of a TWC by the hydrothermal method. A TWC was also prepared by the impregnation method for comparison. The chemical and physical properties as well as the catalytic activities of these catalysts are compared and discussed.

2. Experimental procedures

2.1 Preparation of boehmite

As the precursor of an Al_2O_3 support, boehmite (AlOOH) was prepared by the hydrothermal method. The precursor slurry was prepared by adding a NaOH aqueous solution dropwise to an $\text{Al}_2(\text{SO}_4)_3$ aqueous solution while stirring. The Na/Al molar ratio of the starting materials was 3.0, and the pH of the precursor slurry was 9.6. The prepared precursor slurry was transferred to a 200 ml Teflon-lined stainless-steel autoclave. The autoclave was then sealed and heated at 140°C for 1 h in air while stirring. After completion of the hydrothermal reaction, the resultant slurry was filtered, washed with distilled water, and freeze-dried for 12 h.

2.2 Synthesis of Pt-Rh/ $\text{CeO}_2/\text{Al}_2\text{O}_3$

Pt-Rh/ $\text{CeO}_2/\text{Al}_2\text{O}_3$ catalysts (Pt:Rh: CeO_2 : Al_2O_3 = 0.8:0.2:10:100 weight ratio) were synthesized by the hydrothermal and impregnation methods.

2.2.1 Hydrothermal method

In the hydrothermal method, the precursor slurry was prepared by adding a NaOH aqueous solution dropwise to a slurry containing boehmite (prepared as described above) and cerium nitrate while stirring. The Na/Ce molar ratio of the starting materials was 10.0 and the pH of the precursor slurry was 13.5. The prepared precursor slurry was transferred to a 200 ml Teflon-lined stainless-steel autoclave, which was then sealed and heated at 140°C for 1 h while stirring. After completion of the hydrothermal reaction, the resultant $\text{CeO}_2/\text{AlOOH}$ slurry was mixed with an aqueous solution of HPtCl_3 and RhCl_3 . The pH of the precursor slurry was 13.0. The prepared precursor slurry was transferred to a 200 ml Teflon-lined stainless-steel autoclave, which was then sealed and heated at 140°C for 1 h while stirring. After completion of the hydrothermal reaction, the resultant Pt-Rh/ $\text{CeO}_2/\text{AlOOH}$ slurry was filtered, washed

with distilled water, and freeze-dried for 12 h. The dried powder was subsequently annealed at 500°C for 3 h in air. The obtained Pt-Rh/ $\text{CeO}_2/\text{Al}_2\text{O}_3$ is referred to hereinafter as "Pt-Rh/CA-HT."

2.2.2 Impregnation method

In the impregnation method, the weight ratio of the starting materials for Pt, Rh, Ce, and Al was the same as that in the hydrothermal method. Boehmite (prepared as described above) was mixed with an aqueous solution of cerium nitrate for 4 h while stirring. The obtained slurry was evaporated at 80°C and the dried powder was then annealed at 500°C for 3 h. The obtained $\text{CeO}_2/\text{Al}_2\text{O}_3$ was then mixed with an aqueous solution of HPtCl_3 and RhCl_3 for 4 h while stirring. The finally obtained slurry was evaporated at 80°C , and the dried powder was then annealed at 500°C for 3 h. The obtained Pt-Rh/ $\text{CeO}_2/\text{Al}_2\text{O}_3$ is referred to hereinafter as "Pt-Rh/CA-IM."

2.3 Characterization

The chemical compositions of the catalysts were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on a Seiko Instruments Inc. SPS7800.

The crystalline phases of the catalysts were identified by powder X-ray diffraction (XRD) using a Bruker D8 ADVANCE diffractometer with $\text{Cu K}\alpha$ ($\lambda = 0.15406$ nm) radiation operating at 35 kV and 350 mA. The XRD patterns were collected in the 2θ range from 10 to 80° with a scanning step size of 0.0234° and a scanning speed of 0.13 s/step.

The structures of the catalysts were identified by Raman spectroscopy using a NRS-1000 Raman spectrometer (Jasco Corp.) equipped with a 532 nm green laser. The Raman profiles were collected in the frequency range of $200\text{--}900\text{ cm}^{-1}$ at a resolution of 1 cm^{-1} with an acquisition time of 20 min.

The specific surface areas of the catalysts were measured using the BET method with a Desorb III instrument (Shimadzu Co.).

The oxidation state of the Ce of the samples was evaluated by X-ray photoelectron spectroscopy (XPS) using a JEOL JPS-9010MX spectrometer equipped with $\text{MgK}\alpha$ (1.2536 keV) radiation operating at 10 kV and 10 mA. The XPS profiles were collected with Ce3d and O1s as internal standards and a scan step size of 0.1 eV.

The particle sizes, morphologies, and distributions of the Al, Ce, Pt, and Rh of the samples were investigated using a transmission electron microscope (TEM, JEOL-ARM200F) equipped with a scanning transmission electron microscope (STEM) and energy dispersive X-ray (EDX) analysis capabilities at an accelerating voltage of 200 kV.

The reducibility of the catalysts was evaluated by hydrogen temperature-programmed reduction ($\text{H}_2\text{-TPR}$). As a pre-treatment, 20 mg of the catalyst in a quartz U-tube was annealed at 500°C in He for 1 h at a heating rate of $20^\circ\text{C min}^{-1}$. The reduction reaction was performed under H_2/N_2 (5%) gas while heating from 50 to 700°C at a rate

of 10 °C min⁻¹. The H₂ consumption was detected using a thermal conductivity detector (TCD).

The dispersion of precious metals (Pt and Rh) on the CeO₂/Al₂O₃ surface of the catalysts was determined by CO chemisorption using the CO pulse method. As a pre-treatment, 50 mg of the catalyst was annealed in a quartz U-tube at 500 °C in He for 1 h at a heating rate of 20 °C min⁻¹ and then cooled to room temperature. Subsequently, CO pulses were injected until reaching the breakthrough point, and the CO consumption was detected using a TCD.

2.4 Catalytic activity test

The catalytic activities of the catalysts were evaluated using a fixed-bed flow reactor (Φ 10 mm) made of stainless steel within an atmospheric pressure and a reaction temperature range of 100–400 °C. **Figure 1** shows a schematic illustration of the experimental apparatus for the catalytic activity test. 1.0 ml of the catalyst (0.60 g) was placed in the reactor by packing quartz wool around both ends of the catalyst. The reaction gas was a mixture of CO (0.50%), CO₂ (0.60%), O₂ (0.33%), NO (0.049%), C₃H₆ (0.025%), and N₂ (as a balance gas). The gas hourly space velocity was 24000 h⁻¹. The λ value defined as the oxidant/reductant ratio was calculated using the following formula:

$$\lambda = \frac{2[\text{CO}_2] + [\text{NO}]}{9[\text{C}_3\text{H}_6] + [\text{CO}]}$$

where [CO₂], [NO], [C₃H₆], and [CO] are the concentrations of the various components. In this study, the λ value was 0.96, which indicates a fuel-rich condition.

As a pre-treatment, the catalysts were annealed at 500 °C in N₂ for 1 h at a heating rate of 20 °C min⁻¹. The catalyst bed temperature was increased from 25 to 400 °C at a rate of 2 °C/min. The gas was analyzed online before entering and after passing through the reactor using an Auto 5.1 analyzer (RIELLO JAPAN Inc.), and the NO, CO, and C₃H₆ conversions were calculated using the following formula:

$$\text{Conversion (\%)} = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100$$

Fig. 1. Schematic illustration of the experimental apparatus for the catalytic activity test.

where C_{in} and C_{out} are the gas concentrations of a given component before and after passing through the reactor, respectively.

3. Results and discussion

3.1 Chemical and physical properties

The crystal structures and morphologies of Pt-Rh/CA-HT and Pt-Rh/CA-IM were characterized and compared.

Table 1 shows the expected chemical compositions based on the starting materials used in the impregnation and hydrothermal methods as well as the actual compositions determined using ICP-AES for Pt-Rh/CA-HT and Pt-Rh/CA-IM. The actual Ce content of Pt-Rh/CA-IM and the actual Pt and Rh contents of Pt-Rh/CA-HT and Pt-Rh/CA-IM were in good agreement with the expected values. The actual Ce content of Pt-Rh/CA-HT was larger than the expected value, however indicating that the actual Al/Ce weight ratio was lower than the expected value. This may be due to dissolution of AlOOH during the hydrothermal reaction of CeO₂/AlOOH under basic conditions according to the following reversible reaction:³²⁾

Figure 2 shows the powder XRD patterns of Pt-Rh/CA-HT and Pt-Rh/CA-IM. All of the observed diffraction lines were attributed to the face-centered cubic unit cell of CeO₂ and γ-Al₂O₃ with the Fm-3 m (JCPDS card No. 34-0394) and Fd-3 m (JCPDS card No. 50-0741) space group

Table 1. Expected and actual compositions of Pt-Rh/CA-HT and Pt-Rh/CA-IM

	Ce (wt %)	Pt (wt %)	Rh (wt %)
Expected	7.33	0.72	0.18
Actual (Pt-Rh/CA-IM)	7.22	0.58	0.17
Actual (Pt-Rh/CA-HT)	9.06	0.72	0.22

Fig. 2. Powder XRD patterns of Pt-Rh/CA-HT and Pt-Rh/CA-IM.

Table 2. Lattice parameters and crystallite sizes of CeO₂ and BET surface areas of CeO₂ for Pt-Rh/CA-HT and Pt-Rh/CA-IM

	Lattice parameters of CeO ₂		S_{BET} (m ² g ⁻¹)
	a (Å)	Cry. size (nm)	
Pt-Rh/CA-HT	5.4084(9)	5.8	178
Pt-Rh/CA-IM	5.4131(5)	7.0	184

Fig. 3. Raman profiles of Pt-Rh/CA-HT and Pt-Rh/CA-IM.

symmetries, respectively. As seen in Fig. 2, there was no evidence of impurity phases and crystalline phases of precious-metal (Pt and Rh) species. This may be due to the low crystallinity of the precious-metal species in the catalysts. Based on the ICP-AES and XRD results, Pt-Rh/CeO₂/Al₂O₃ was successfully synthesized by the hydrothermal and impregnation methods.

Table 2 lists the lattice parameters and crystallite sizes of CeO₂ calculated using the Rietveld method as well as the BET surface area of CeO₂. The lattice parameters of CeO₂ for Pt-Rh/CA-HT and Pt-Rh/CA-IM were $a = 5.4084(9)$ Å and $5.4131(5)$ Å, respectively. These values are consistent with JCPDS card No. 34-0394 ($a = 5.411$ Å) and with the JCPDS record (card No. 34-0394, $a = 5.411$ Å). The crystallite size and BET surface area of CeO₂ for Pt-Rh/CA-HT were slightly smaller than those for Pt-Rh/CA-IM.

Raman spectroscopy measurements were conducted to further characterize the structures. **Figure 3** shows the Raman profiles for Pt-Rh/CA-HT and Pt-Rh/CA-IM. Broad peaks at 465, 569, and 663 cm⁻¹ for Pt-Rh/CA-HT and a strong peak at 461 cm⁻¹ as well as a broad peak at 656 cm⁻¹ for Pt-Rh/CA-IM were observed. These Raman profiles are consistent with those reported previously by Wu et al.³³⁾ The peaks at 465 cm⁻¹ for Pt-Rh/CA-HT and 461 cm⁻¹ for Pt-Rh/CA-IM were assigned to the F_{2g} mode of cubic CeO₂.^{34)–38)} In a previous study, the Raman peaks at 550 and 690 and 560 and 690 cm⁻¹ were assigned to Pt–O–Ce and Rh–O–Ce vibrations, respectively.³⁸⁾ The peaks at 569 and 663 cm⁻¹ for Pt-Rh/CA-HT and at 656

Fig. 4. Ce3d XPS profiles of (a) Pt-Rh/CA-HT and (b) Pt-Rh/CA-IM and calculated profiles (v , v' , v'' , v''' , u , u' , u'' , and u''').

cm⁻¹ for Pt-Rh/CA-IM were therefore assigned to M–O–Ce ($M = \text{Pt, Rh}$) vibrations. As seen in Fig. 3, Pt-Rh/CA-HT exhibited a lower intensity ratio ($I_{\text{CeO}_2}/I_{\text{M–O–Ce}}$, $M = \text{Pt, Rh}$) than Pt-Rh/CA-IM. This indicates that the ratio of CeO₂ coating by Pt and Rh species for Pt-Rh/CA-HT was higher than that for Pt-Rh/CA-IM.

The oxidation states of the surface species of the catalysts were characterized by XPS. **Figure 4** shows the Ce3d XPS profiles for Pt-Rh/CA-HT and Pt-Rh/CA-IM. As seen in Fig. 4, Pt-Rh/CA-HT and Pt-Rh/CA-IM exhibited similar Ce3d XPS profiles, which comprised eight peaks that were assigned to Ce3d_{5/2} (v , v' , v'' , and v''') and Ce3d_{3/2} (u , u' , u'' , and u''') of Ce⁴⁺ and Ce³⁺ species. Based on the Ce3d XPS profiles, the Ce³⁺ contents of Pt-Rh/CA-HT and Pt-Rh/CA-IM were calculated from the peak area ratio of Ce⁴⁺ 3d_{5/2} (v , v'' , and v''') and Ce³⁺ 3d_{5/2} (v') using the following formula:

$$\text{Ce}^{3+} (\%) = \frac{A_{v'}}{A_v + A_{v''} + A_{v'''}} \times 100$$

where A_v , $A_{v''}$, $A_{v'''}$, and $A_{v'}$ are the peak areas of Ce⁴⁺ 3d_{5/2} (v , v'' , and v''') and Ce³⁺ 3d_{5/2} (v'). The calculated

Fig. 5. STEM images of (a-b) Pt-Rh/CA-HT and (c-d) Pt-Rh/CA-IM.

Fig. 6. STEM image of Pt-Rh/CA-HT and the corresponding EDX line scan profiles of Ce, Pt, and Rh.

Ce³⁺ contents of Pt-Rh/CA-HT and Pt-Rh/CA-IM were 33 and 28%, respectively. This indicates that the oxidation state of Ce in Pt-Rh/CA-HT is similar to that in Pt-Rh/CA-IM.

The particle sizes and morphologies of CeO₂, γ -Al₂O₃, Pt, and Rh in the catalysts were investigated using TEM. **Figure 5** shows the STEM images of Pt-Rh/CA-HT and Pt-Rh/CA-IM. The particle size and morphology of CeO₂ and the distribution of Pt and Rh for Pt-Rh/CA-HT were quite different from those for Pt-Rh/CA-IM. Hexagonal γ -Al₂O₃ nanoplates 10–30 nm in diameter, hollow CeO₂ nanorods 5–8 nm in diameter and 30–50 nm in length, and Pt-Rh nanoparticles less than 1 nm in diameter were observed in Pt-Rh/CA-HT. EDX line scan analysis was conducted to further characterize the CeO₂ nanorods. **Figure 6** shows the STEM image of Pt-Rh/CA-HT and the corresponding EDX line scan profiles of Ce, Pt, and Rh. Interestingly, as seen in Fig. 6, the center of the CeO₂ nanorod exhibited lower Ce, Pt, and Rh counts than the surface. In addition, as seen in Fig. 5, CeO₂ primary nanoparticles 2–5 nm in diameter were observed on the CeO₂ nanorods of Pt-Rh/CA-HT. The hollow CeO₂ nanorods in Pt-Rh/CA-HT are coated with nanoparticle arrays as a result. On the other hand, γ -Al₂O₃, CeO₂, and Pt-Rh nanoparticles were observed in Pt-Rh/CA-IM, and the corresponding particle sizes were 10–20, 3–5 nm, and less than 1 nm in diameter, respectively. The primary particle sizes of CeO₂ for Pt-Rh/CA-HT and Pt-Rh/CA-IM were approximately the same as the corresponding crystallite sizes calculated using the Rietveld method. In addition, Pt-Rh nanoparticles were observed only on the CeO₂ surface of Pt-Rh/CA-HT, whereas they were observed on both the Al₂O₃ and CeO₂ surfaces of Pt-Rh/CA-IM. These results indicate that hydrothermally synthesized Pt-Rh/CeO₂/Al₂O₃ catalysts can serve as selective supports for Pt and Rh on CeO₂ surfaces and that they are in good agreement with the Raman spectroscopy data.

Fig. 7. STEM images of (a) Pt-Rh/CA-HT and (b) Pt-Rh/CA-IM and the corresponding elemental maps of Al, Rh, Ce, and Pt.

EDX analyses and elemental mapping were performed to characterize the distribution of Ce, Pt, and Rh using TEM. **Figure 7** shows the STEM images of Pt-Rh/CA-HT and Pt-Rh/CA-IM and the corresponding elemental maps of Al, Rh, Ce, and Pt. The distribution of Pt and Rh in Pt-Rh/CA-HT was different from that in Pt-Rh/CA-IM; Pt and Rh were uniformly distributed along with only Ce in Pt-Rh/CA-HT but along with both Al and Ce in Pt-Rh/CA-IM. These results are in good agreement with the STEM images.

The reducibility of Pt, Rh, and CeO_2 in the catalysts was evaluated using H_2 -TPR. **Figure 8** shows the H_2 -TPR profiles of Pt-Rh/CA-HT and Pt-Rh/CA-IM. Very weak peaks at 146°C and around 700°C for Pt-Rh/CA-HT and a

weak peak at 128°C as well as strong peaks at 481 and 632°C for Pt-Rh/CA-IM were observed. The peaks at 146°C for Pt-Rh/CA-HT and at 128°C for Pt-Rh/CA-IM were attributed to the reduction in PtO_x and RhO_x species,^{38)–44)} and the peaks at around 700°C for Pt-Rh/CA-HT and at 481 and 632°C for Pt-Rh/CA-IM to the reduction in CeO_2 .^{38),43),44)} These results indicate that reduction of CeO_2 is more difficult for Pt-Rh/CA-HT than that for Pt-Rh/CA-IM, despite the similar oxidation state of Ce characterized by XPS. This may be due to a higher ratio of CeO_2 coating by Pt and Rh species for Pt-Rh/CA-HT than that for Pt-Rh/CA-IM.

Because the dispersion of Pt and Rh strongly affects the catalytic activities of the catalysts,^{17),19)} CO chemisorption

Fig. 8. H₂-TPR profiles of Pt–Rh/CA-HT and Pt–Rh/CA-IM.

on Pt–Rh/CA-HT and Pt–Rh/CA-IM was analyzed using the CO pulse method. The amount of CO chemisorption on Pt–Rh/CA-HT was 0.559 ml g^{−1}, which was much higher than that on Pt–Rh/CA-IM (0.147 ml g^{−1}). This result suggests that the hydrothermal method significantly improves Pt and Rh dispersion compared with the impregnation method.

3.2 Catalytic activity

The catalytic activities of Pt–Rh/CA-HT and Pt–Rh/CA-IM were evaluated. **Figure 9** shows the NO, CO, and C₃H₆ conversions as a functions of the reaction temperature for Pt–Rh/CA-HT and Pt–Rh/CA-IM. As seen in Fig. 9, the NO, CO, and C₃H₆ conversions of Pt–Rh/CA-HT and Pt–Rh/CA-IM increased with increases in the reaction temperature. NO conversion began at 160°C for both Pt–Rh/CA-HT and Pt–Rh/CA-IM, ultimately achieving 100% conversion at 280 and 300°C for Pt–Rh/CA-HT and Pt–Rh/CA-IM, respectively. C₃H₆ conversion began at 220 and 200°C for Pt–Rh/CA-HT and Pt–Rh/CA-IM, respectively, moreover, and their corresponding 100% conversion temperatures were 260 and 280°C. These results indicate that the catalytic activities of Pt–Rh/CA-HT and Pt–Rh/CA-IM for NO reduction and C₃H₆ oxidation were similar. On the other hand, CO conversion began at 120 and 160°C for Pt–Rh/CA-HT and Pt–Rh/CA-IM, respectively, and their corresponding 100% conversion temperatures were 300 and 340°C. The lights-off temperatures (temperature at 50% conversion) of CO were 180 and 240°C, moreover, for Pt–Rh/CA-HT and Pt–Rh/CA-IM, respectively. These results indicate that the conversion temperature of CO is the lowest among NO, CO, and C₃H₆, a result is consistent with that of a previous study by Ozawa et al.⁸⁾ These results also indicate that Pt–Rh/CA-HT exhibits higher catalytic activity for CO oxidation than Pt–Rh/CA-IM. This is due to the difference in the dispersion of Pt and Rh between Pt–Rh/CA-HT and Pt–Rh/CA-IM.

Fig. 9. (a) NO, (b) CO, and (c) C₃H₆ conversions as functions of the reaction temperature for Pt–Rh/CA-HT and Pt–Rh/CA-IM.

4. Conclusions

A Pt–Rh/CeO₂/Al₂O₃ TWC comprising hollow CeO₂ nanorods coated with nanoparticle arrays has been successfully synthesized using the hydrothermal method. Hydro-

thermally synthesized Pt–Rh/CeO₂/Al₂O₃ catalysts served as selective supports for Pt and Rh on CeO₂ surfaces. Although the lights-off temperatures of NO and C₃H₆ were similar for Pt–Rh/CeO₂/Al₂O₃ catalysts synthesized by the hydrothermal and impregnation methods, Pt–Rh/CeO₂/Al₂O₃ synthesized by the hydrothermal method exhibited a lower lights-off temperature for CO than that synthesized by the impregnation method. The better catalytic activity of Pt–Rh/CeO₂/Al₂O₃ synthesized by the hydrothermal method was attributed to its better dispersion of Pt and Rh compared with the impregnation method.

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