Improved activity and durability of Rh-based three-way catalyst under diverse aging atmospheres by ZrO₂ support

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ABSTRACT

The catalytic activity and durability of Rh/ZrO₂ catalyst were investigated compared with Rh/Al₂O₃ catalyst under diverse aging atmospheres, including lean, rich and lean–rich cyclic aging atmospheres, to simulate the real working conditions of three-way catalyst. Oxidation states and microstructures of rhodium species were investigated to correlate with the catalytic performance of the catalysts. The catalytic performance and durability of the Rh catalyst under diverse aging atmospheres were drastically enhanced by ZrO₂ support. ZrO₂ support was confirmed to be able to effectively inhibit rhodium sintering even under diverse aging conditions. It can also successfully keep Rh species in an active low-valence state on the surface of the catalyst. The superiority of ZrO₂ support compared to Al₂O₃ was verified by the Rh-based monolith catalyst.

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Introduction

The three-way catalysts (TWCs) converter is the most effective catalytic system for removing air pollutants emitted from gasoline engines (Di Monte et al., 2000; Heck et al., 2009; Wang et al., 2008; Zhan et al., 2014). The modern commercial TWCs are generally composed of active precious metals (PMs) such as palladium (Pd) and rhodium (Rh), Al₂O₃, CeₓZr₁₋ₓO₂ and other oxides to simultaneously remove CO, HCs and NOₓ (Ferrer et al., 2015; Kang et al., 2014; Wang et al., 2010). Especially Rh is indispensable for converting NOₓ into N₂ in high-performance TWCs (Gandhi et al., 2003; Nagao et al., 2015). Although the technologies of TWCs are well-established, further improvement of catalytic efficiency and stability is still required to meet the more and more stringent regulations for automotive emission control.

The efficiency of catalysts mainly depends on the dispersion and oxidation state of active PMs in the catalysts (Yang et al., 2008; Zhan et al., 2014), and in most cases catalysts are damaged due to the sintering of PMs and the formation of alloys between PMs themselves as well as thermal agglomeration of catalyst supports at high temperatures (Cao et al., 2015; Hietikko et al., 2004; Lassi et al., 2004; Nagao et al., 2015). Understanding the deactivation process of PM catalysts and their aging-resistance property may provide guidance for the developing strategies of advanced TWCs. Take Rh/Al₂O₃ catalysts for example, thermal deactivation of Rh/Al₂O₃ catalysts was considered as one of the main bottleneck problems to restrict their durability, though alumina is the most commonly used support material for PMs. Rhodium undergoes a deleterious high-temperature interaction with alumina to form rhodium aluminate under oxidizing conditions and irreversibly diffuses into the alumina phase.

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(Hwang et al., 1999; Stoyanovskii et al., 2009), while Rh species exists in relatively smaller particles under an inert or reducing atmosphere (Zhao et al., 2014). On the basis of these well-studied phenomena, many efforts have been made to improve both the activity and durability of rhodium-based catalysts. Seeking the alternative support materials is one of the effective attempts. Among the candidate supports, ZrO$_2$ has been regarded as a beneficial support material for Rh up to now. Yao et al. (1980) demonstrated that the phase of Rh supported on pure ZrO$_2$ was thermally stable, and the activity of the Rh/ZrO$_2$ catalyst for the NO + H$_2$ reaction had little decrease even undergoing thermal aging at 950 °C. Heo et al. (2012) also claimed that Rh/ZrO$_2$ catalyst displayed better thermal durability in comparison to Rh/Al$_2$O$_3$ and Rh/CeO$_2$. The authors proposed that the high thermal durability might be related to the helpful interaction between Rh and ZrO$_2$ which could prevent the diffusion of Rh into ZrO$_2$ lattice during thermal aging.

However, the practical property of a candidate catalyst should be verified under diverse working conditions, as the actual serving environment of TWCs is always complex due to the fluctuating operating condition during vehicle driving. Accordingly, to assess the durability of a target catalyst under specific operating conditions, thermal aging under different atmospheres is typically used to simulate the actual working environment of the catalysts (Cao et al., 2013). With this respect, the advantage of ZrO$_2$ support compared to alumina under diverse simulated working conditions is essential to be systematically studied.

In this work, the catalytic activity and durability of the Rh/ZrO$_2$ catalyst are investigated compared with the Rh/Al$_2$O$_3$ catalyst under diverse aging conditions, including lean, rich and lean-rich cyclic aging, to simulate the real working condition of TWCs. The features of rhodium species are studied by investigating oxidation states and microstructures. The catalytic performance of monolith catalyst is also studied based on the concept of Rh/ZrO$_2$ model catalyst.

1. Experimental

1.1. Catalyst preparation

Rh/ZrO$_2$ (RZ) powder catalyst was prepared by incipient-wetness impregnation with Rh(NO$_3$)$_3$ as precursor on ZrO$_2$ (Z, La stabilized ZrO$_2$: ZrO$_2$/La$_2$O$_3 = 92/8$, $S_{\text{BET}} = 75$ m$^2$/g) materials. The metal loading of Rh was 0.5 wt.%. After drying at 110 °C for 12 hr, the samples were calcined at 550 °C for 3 hr in static air in a muffle to obtain the fresh catalysts (RZ). Aged catalysts were prepared by treating the fresh catalysts under different aging conditions: (1) air (lean), (2) H$_2$ (rich, 7% H$_2$ in N$_2$) or (3) cyclic air-H$_2$ (lean-rich cycle: 10 min air, 8 min N$_2$, 10 min 4% H$_2$ in N$_2$, 8 min N$_2$, 10 min steam) at 1050 °C for 12 hr. The 0.5 wt.% Rh/Al$_2$O$_3$ (RA, Al$_2$O$_3$: $S_{\text{BET}} = 150$ m$^2$/g) catalyst was also prepared by the same procedure and aged under different aging conditions for reference.

The double-layered monolith catalysts were prepared by the sequential washcoating of the Pd/Al$_2$O$_3$ and then Rh-based catalysts onto a cylindrical cordierite monolith substrate ($V = 0.3016$ dm$^3$). The loading of each layer is 100 g catalyst/L. The loading amounts of palladium and rhodium are 1 and 0.1 g/L, respectively.

1.2. Catalyst characterization

The specific surface areas of the samples were measured using the N$_2$ adsorption at −196 °C by the four-point Brunauer–Emmett–Teller (BET) method on an automatic surface analyzer (F-Sorb 3400, Gold APP Instrument, China). Prior to the measurements, the samples were degassed in vacuum at 200 °C for 2 hr.

Rhodium dispersion of the catalysts was characterized on Micromeritics Auto Chem II 2920 apparatus (USA) with a thermal conductivity detector (TCD). For each experiment, approximately 100 mg catalyst was placed in a U-shaped quartz tube (i.d. = 10 mm) and reduced in a flow of 10% H$_2$/Ar while ramping the temperature up to 400 °C at the rate of 10 °C/min, and then held at 400 °C for 30 min in flowing He (50 °C/min) for proper degassing. After that the sample was cooled down to 25 °C, the loop gas of 10% CO/He was pulsed over the sample and the TCD signal was recorded until the peak area became constant. The percent dispersion was calculated by dividing the number of exposed surface Rh atoms (as determined by CO chemisorption) by the total amount of Rh in the catalyst according to the equations listed in our previous study (Cao et al., 2016).

Transmission electron microscopy (TEM) images were captured on a JEOL 2100 electron transmission microscope (JEOL Ltd., Japan). The contrast of rhodium and zirconia-containing support is very similar under TEM observations. For a better observation, all the catalysts were reduced in 10% H$_2$/Ar at 350 °C for 30 min before TEM observation. For the sample preparation, the samples were crushed in an agate mortar and suspended in ethanol. After ultrasonic dispersion, a droplet was deposited on a copper grid supporting a perforated carbon film. The mean Rh particle size was determined by analyzing 50 particles per sample.

X-ray photoelectron spectroscopy (XPS) experiments were carried out on an ESCALAB 250Xi system (Thermo Fisher Scientific, USA) equipped with a monochromatic Al K$_\alpha$ X-rays (1486.8 eV) and the samples were measured under ultrahigh vacuum (−10$^{-9}$ Pa). Prior to the measurements, the samples were degassed in vacuum at room temperature for 1 hr. Sample charging during the measurement was compensated by an electron flood gun. The electron take off angle was 45° with respect to the sample surface. The analyzer was operated using an analysis area of approximately 500 μm in diameter. The XPS data from the regions related to the Rh3$d$ core levels were recorded. All binding energies were calibrated using the C 1s carbon peak (284.6 eV).

1.3. Catalytic activity measurement

The 100 mg catalyst was diluted with 300 mg quartz sands to prevent a reaction runaway. The mixture was loaded in a quartz reaction tube with the diameter of 10 mm. The catalytic activity of the catalysts was evaluated by passing a gas mixture of 5000 ppm CO, 5000 ppm NO and N$_2$ in balance. The space velocity was 12,000 hr$^{-1}$. The reactor was heated from RT to 500 °C at a heating rate of 10 °C/min after N$_2$.
pretreatment at 500 °C for 30 min. The outlet gas from the reactor was analyzed by an FT-IR gas analyzer (Thermo Fisher Nicolet Is10, Thermo Fisher Scientific, USA). The catalytic performance of the monolith catalysts were tested at $T = 500$ °C for 48 hr under the same reaction atmosphere.

2. Results and discussion

2.1. Catalytic activity

The catalytic reduction of NO by CO makes a good model reaction to simulate the reaction in real automotive emissions purification (Cao et al., 2015; Ferrer et al., 2015; Ozensoy and Goodman, 2004). The catalytic activity of RZ and RA before and after high-temperature aging for CO–NO reaction was measured. NO light-off curves of the catalysts are comparatively listed in Fig. 1. The light-off curves and $T_{50}$ values (the temperature at which 50% conversion is obtained) of CO (shown in Table 1) were quite close to those of NO for all the samples. The catalytic activity was effectively influenced by support materials as well as aging atmosphere. As shown in Fig. 1, the ZrO$_2$ supporting samples exhibited better activities than the Al$_2$O$_3$ supporting ones, especially after air and cyclic aging. For the fresh sample, RZ possessed a better catalytic activity with $T_{50} = 195$ °C compared with $T_{50} = 240$ °C of RA. And the superiority of RZ was magnified especially after air and cyclic aging, for which the $T_{50}$ values of RZ samples were about 100 °C lower than those of RA samples. It suggests that certain differences of the rhodium particles appear between ZrO$_2$ supporting and Al$_2$O$_3$ supporting catalysts, especially under diverse aging atmospheres.

2.2. Dispersion and particle size of rhodium

The dispersion and particle size of rhodium are considered as one of the crucial factors for the activity of rhodium catalyzed reactions (Brinen et al., 1975; Gatica et al., 2000). TEM images were used to identify the particle size and dispersion of the rhodium particles. The particle sizes obtained from TEM images are listed in Table 1, and the typical TEM images together with the size distribution of Rh particles in the aged catalysts are shown in Fig. 2. Since the samples were pre-reduced prior to the TEM observation, most rhodium particles existed in metallic state. The particles labeled by red arrows in Fig. 2 were identified to be rhodium particles. Rhodium particles were finely dispersed in the fresh samples. For the aged RZ samples, the rhodium particles grew to 4–11 nm in the following sequence: air-aged (11 nm) > H$_2$-aged (5.2 nm) > cyclic-aged (4.1 nm). The d-spacing values of rhodium species in the RZ samples were (0.217 ± 0.003) nm, (0.221 ± 0.003) nm and (0.218 ± 0.003) nm in air-aged RZ, H$_2$-aged RZ and cyclic-aged RZ, respectively, as shown in the inserted figures. The values were consistent with that of the spacing along the (111) plane of Rh (0.2197 nm), confirming the metal state of Rh species. Additionally, the d-spacing
value of 0.293 nm in Fig. 2a is close to that of the spacing along the (111) plane of t-ZrO₂ (0.2950 nm). The interaction zones between rhodium and the support in Fig. 2a indicate the presence of rhodium–support interactions. Comparatively, the particle size of rhodium particles in RA was times larger than that in RZ after air and cyclic aging, while the Rh particle size in H₂-aged RA was comparable with that in H₂-aged RZ. It demonstrates that the ZrO₂ support, compared to Al₂O₃ support, can effectively inhibit the sintering of rhodium nanoparticles under all conditions (lean, rich, lean–rich).

CO uptake values of the catalysts were measured by CO chemisorption technique as shown in Table 1. The corresponding Rh dispersion and Rh particle sizes calculated by assuming a stoichiometry of 1.0 CO/Rh (Haneda et al., 2010) are also displayed in Table 1. The CO uptakes were apparently different although all the samples have a same total content of Rh. The CO uptake on the fresh sample was extremely high and the dispersion was larger than 1. It was related to the gem-dicarbonyl species (two molecules of CO are coordinated to one Rh center) on very small nanoparticles as CO/Rh ratio increased with decreasing Rh crystallite size (Cavanagh and Yates, 1981). For the aged RZ samples, the CO uptake varied with the aging atmosphere in the following sequence: air-aged (7.5 μmol/g catalyst) < H₂-aged (8.7 μmol/g catalyst) < cyclic-aged (13.6 μmol/g catalyst). Correspondingly, the dispersion of Rh was in the same order, and the deduced particle sizes of
rhodium were in good agreement with the TEM results. For the aged RA samples, the CO uptakes and Rh dispersion on air-aged and cyclic-aged RA were fairly small, indicating severe sintering of rhodium and loss of active adsorption sites on rhodium surface. It has been reported (Hwang et al., 1999; Zhao et al., 2014) that the oxygen-containing atmosphere induced a strong interaction between Rh species and the Al2O3 support, which resulted in a severe sintering of particles of Rh species and the formation of inactive rhodium–aluminate species. The current results demonstrate that the ZrO2 support is beneficial to preserving small rhodium particles with high dispersion under all the aging conditions (lean, rich, lean–rich), which confirms that the ZrO2 support should be a better support for rhodium which can effectively inhibit the sintering of Rh species in comparison to the alumina support.

2.3. Oxidation state of surface rhodium species

The X-ray photoelectron spectra (XPS) measurement was performed to determine the oxidation state and dispersion of rhodium on the surface of the catalysts. Fig. 3 shows the XPS results in the binding energy (B.E.) range of Rh 3d spectra including Rh 3d5/2 and 3d3/2 peaks. The surface contents of rhodium species in the samples are also included in Fig. 3. After aging, the surface Rh atomic contents of the catalysts obviously decreased in comparison to the corresponding fresh sample, which is possibly related to sintering of rhodium species or diffusion of rhodium into the support. It can be noted that the surface Rh contents in the fresh samples were lower than those in the H2-aged samples, especially for RA catalyst. It may be related to the limited detection depth (<10 nm) of XPS technique, since the percentage of Rh atoms in the several atomic layers, which the soft X-ray employed in XPS can penetrate, is lower in the fresh samples considering the times-larger specific surface area compared with the H2-aged samples as listed in Table 1 (Zhao et al., 2014). For the aged RZ sample, the surface Rh atomic contents, as listed in Fig. 3a, were in the following sequence: H2-aged (0.38%) > cyclic-aged (0.26%) > air-aged (0.13%). The lowest surface Rh content in the air-aged RZ indicated that the rhodium species may partially diffuse into the ZrO2 support under oxidative conditions. However, the surface Rh content in the cyclic-aged RZ tended to be restored compared with air-aged RZ, indicating that the restoration of surface Rh content on ZrO2 support may occur under reductive condition. For the aged RA samples, the surface Rh contents followed the sequence of H2-aged (0.61%) > air-aged (0.13%) > cyclic-aged (0.10%). The dramatic decrease of surface Rh content in the air-aged and cyclic-aged RA catalysts was attributed to the sintering of rhodium particles and formation of the metal-support interphase such as Rh(AlO2) under oxidative conditions (Yao et al., 1980; Zhao et al., 2014). The very similar Rh content in air-aged and cyclic-aged RA demonstrated that once the Rh was incorporated into alumina under oxidative conditions, the restoration of metallic Rh from the Rh aluminate hardly occurred under the reductive atmosphere. In this respect, ZrO2 support performs better in keeping more surface rhodium species.

XPS spectra of Rh 3d in the samples were fitted using 6 peaks. The peaks were marked as u and v’ for Rh6 3d5/2 (306.8–307.5 eV) and 3d3/2, v and v’ for Rh3+ 3d5/2 (308.8–309.1 eV) and 3d3/2, w and w’ for Rh4+ 3d5/2 (309.6–310.1 eV) and 3d3/2, respectively (Lassi et al., 2004; Zhao et al., 2014). Rh6 and Rh3+ are catalytic active species due to their easier redox property compared with the Rh4+ species (Oh and Carpenter, 1983) and low valence rhodium species (Rh3+ > Rh4+) is beneficial for the reaction (Araya et al., 2002; Oh and Eickel, 1991). The quantitative data based on the fitted XPS spectra are presented in Table 1. In the fresh RZ and RA samples, the total ratios of catalytic active Rh6 and Rh3+ species were 82.6% and 78.6%, respectively. After air aging, the ratio of Rh4+ species increased. The total ratio of Rh6 and Rh3+ species in air-aged RZ was 78.8%, which was much higher than that in the air-aged RA sample (64%). There was still a high amount of Rh6 species in the air-aged RZ (35.9%), while no Rh6 was detected in the air-aged RA. For the H2-aged samples, all of the rhodium species existed in Rh6 and Rh3+, among which the dominant species was Rh6. After cyclic aging, high Rh4+ ratios were obtained, which was similar with those after air aging. The total ratio of Rh6 and Rh3+ species, which was catalytically active, in the cyclic-aged RZ was also higher than that in the cyclic-aged RA. It demonstrated that the ZrO2 support was beneficial to keep rhodium species in lower oxidative state under all working conditions, which played important roles during rhodium catalysis. None of metallic Rh content was detected in the air-aged and cyclic-

![Fig. 3 – XPS spectra of Rh 3d in RZ (a) and RA (b) catalysts.](image-url)
aged RA, and the Rh species presented mainly as Rh$^{3+}$ and Rh$^{4+}$, indicating that Rh is easily oxidized on Al$_2$O$_3$ support under air and cyclic aging conditions.

2.4. Durability of monolith catalysts

Both aging condition and support materials effectively influence the catalytic activity via adjusting the states of Rh species, as well as their chemical environment. Low-valence rhodium species ($\text{Rh}^0 > \text{Rh}^{3+} > \text{Rh}^{4+}$, “>” means “better than”) as well as high dispersion is beneficial for the CO-NO probe reaction (Araya et al., 2002; Oh and Eickel, 1991), which was also confirmed by our study as shown in Table S1 and Fig. S1. In the present study, we demonstrate that Rh/ZrO$_2$ model catalyst exhibits excellent aging-resistance under kinds of working atmospheres compared with Rh/Al$_2$O$_3$ model catalyst. As demonstrated by TEM and XPS results, rhodium particles in Rh/Al$_2$O$_3$ can be kept in small sizes only under rich atmosphere (H$_2$) when most rhodium species exists in metallic state. It is related to the low vapor pressure of metallic rhodium, which can effectively retard the sintering of metallic rhodium particles (Samsonov, 2013). However, rhodium oxide species strongly interact with alumina support under oxygen-containing atmosphere (lean, lean-rich), which results in the formation of inactive rhodium-aluminate species with high Rh oxidation state (Hwang et al., 1999; Zhao et al., 2014) and the severe sintering of rhodium particles. Compared with alumina support, zirconia can effectively inhibit the sintering of rhodium particles through the rhodium-ZrO$_2$ interaction in either oxidative or reductive atmosphere but avoid the formation of rhodium-support compounds, which has been demonstrated in our study and previous literatures (Heo et al., 2012). Moreover, as demonstrated by XPS results, ZrO$_2$ is able to maintain the highly reactive oxidation state of rhodium under all aging conditions (lean, rich, lean-rich).

Based on the above concept, double-layered monolith catalysts were designed and the catalytic activity was characterized by the same probe reaction. The durability of the prepared monolith catalysts were tested under CO-NO reaction for 48 hr. The CO and NO conversions as dependences of time are shown in Fig. 4. The RZ deposited monolith catalyst showed better stability for both NO and CO conversions. In contrast, the CO conversion on RA deposited monolith catalyst decreased by ~2.8% after 48 hr reaction. The decrease of conversion on RA deposited monolith catalyst was not that large considering the prolonged reaction time, but the decrease was relatively obvious compared with the RZ deposited catalyst. In this sense, RZ deposited monolith catalyst showed superior stable performance. It verifies that ZrO$_2$ is a superior support for rhodium than alumina-based support material.

3. Conclusions

The catalytic performance and durability of both the powder and the monolith Rh catalysts under diverse aging atmosphere were drastically enhanced by ZrO$_2$ support. The sintering of rhodium nanoparticles was effectively inhibited by ZrO$_2$ support under high-temperature aging in either oxidative or reductive atmosphere. The particle size of rhodium particles in Rh/ZrO$_2$ was times smaller than that in RA especially after air and cyclic aging. Moreover, ZrO$_2$ can keep more surface rhodium species and stabilize the surface of Rh species in a relatively reductive state compared to Al$_2$O$_3$ support. These results verify the superiority and applicability of ZrO$_2$ as a catalyst support for rhodium.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2016.04.017.
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