

Effects of CuO-CeO₂ Addition on Structure and Catalytic Properties of Three Way Catalysts

Nguyen The Luong^{1*}, Nguyen Duy Tien¹, Eiji Yamasue², Hideyuki Okumura², Keiichi N. Ishihara²

¹Department of Internal Combustion Engine, School of Transportation Engineering, Hanoi University of Science and Technology, Hanoi, Vietnam

²Department of Socio-Environmental Energy Science, Graduate School of Energy Science, Kyoto University, Kyoto, Japan

Email: *luong.nguyenthe@hust.edu.vn

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Abstract

The noble metals (Pt, Pd, Rh) supported on Cu-Ce mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate were investigated as catalytic performance of Three Way Catalysts (TWC) under simulated automotive exhaust feed gas. The structural, morphological features and catalytic activity were observed by X-ray diffractometry (XRD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET), X-ray photoelectron spectroscopy (XPS) and GC-TCD (Varian CP-4900). The catalytic performance of noble metals (Pt, Rh, Pd) supported on Cu-Ce mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate was compared with noble metals (Pt, Rh, Pd) supported on Ce-Zr mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate and only γ -Al₂O₃ washcoat/FeCrAl substrate at various stoichiometric ratio of oxygen. The results showed that the addition of Cu-Ce mixed oxides improved CO oxidation reaction at lower temperature during stable lambda of 1, the highest CO conversion of 99% is observed for the noble metals (Pt, Pd, Rh) support on Cu-Ce with γ -Al₂O₃ washcoat/FeCrAl substrate. The results also showed that, the addition of Cu-Ce mixed oxides promoted released oxygen, thus it improved strongly CO and C₃H₈ conversion at lean oxygen stoichiometric operation.

Keywords

Three-Way Catalysts (TWCs), Noble Metals, γ -Al₂O₃ Washcoat, CuO-CeO₂, CeO₂-ZrO₂

1. Introduction

Three way catalysts (TWCs) are capable of simultaneous converting CO, hydrocarbon (HC) and nitrogen oxides (NO_x) into harmless CO₂, H₂O and N₂. In TWCs, some noble metals, such as Pt, Rh and Pd act as the active components.

Oxygen storage capacity (OSC) is one of the crucial factors for the performance of TWCs, and the higher OSC promotes the better dynamic performance of catalysts in converting CO, HC and NO_x under conditions from rich to lean A/F (λ -value) in automotive. CeO₂-ZrO₂ solid solution is well-known as an excellent supporter for OSC [1]. CeO₂ exhibits oxygen storage/release behavior by the redox reaction of Ce ions between Ce³⁺ and Ce⁴⁺ [2], and the introduction of ZrO₂ into CeO₂ improves the reduction temperature of CeO₂ through structural modification of CeO₂ [3]. Among many studies on CeO₂ based materials such as CeO₂-Al₂O₃ [4], CeO₂-SiO₂ [5], CeO₂-La₂O₃ [3] [6] [7], CeO₂-TbO_x [8], and CeO₂-PrO_x [9] have been reported to improve OSC and increase the thermal stability.

As legislation becomes tighter, it is necessary to improve the efficiency of TWCs at lower temperatures and under oxygen-rich atmospheres. The copper/copper oxides as CuMO (M = Al, Fe, Mn, Ga) [10] have been found with its oxygen storage/release behavior at lower temperatures. Recently, it was found by authors that CuO-CeO₂ prepared by mechanical milling shows excellent OSC at lower temperatures [11], and it showed higher value of total OSC due to the valence change between Ce⁴⁺/Ce³⁺ and Cu²⁺/Cu⁺/Cu. So it is necessary to know the effect of noble metals supported on Cu-Ce mixed oxides with alumina washcoat. Many reports based on the thermal stability and catalytic performance of noble metals coated on CeO₂-ZrO₂ or coated on γ -Al₂O₃ which supported for traditional TWCs was shown in previously reported [12] [13] [14]. H. He *et al.* reported the performance and redox properties of Pd, Pt, Rh loaded Ce_{0.6}Zr_{0.35}Y_{0.05}O₂ [12]. The aim of this study is to investigate catalytic performance of noble metals supported on Cu-Ce mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate. The catalytic performance of noble metals (Pt, Rh, Pd) supported on Cu-Ce mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate will be compared with noble metals (Pt, Rh, Pd) supported on Ce-Zr mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate and γ -Al₂O₃ washcoat/FeCrAl substrate.

2. Experimental Section

2.1. Catalysts Preparation

Powdery CuO, CeO₂ (Kojundo Chemical) and γ -Al₂O₃, ZrO₂ (Nilaco Corporation) were used as starting materials. The powder mixture of CuO-CeO₂ (50 mol% of CuO content) and CeO₂-ZrO₂ (20 mol% of ZrO₂ content) were milled by using a high-energy vibratory ball milling up to 18 hours (dry milling).

The Fe-Cr (17 - 21 wt%)-Al (2 - 4 wt%) alloy sheet (Nilaco Corporation) was used as the substrate. In order to achieve good adhesiveness between the substrate and the washcoat layer, the substrate was first immersed in an HCl solution (69 wt%) for 2 - 3 min to increase the roughness, followed by immersion in an HNO₃ solution (68 wt%) at 80°C for 5 min to clean the superficial oxide. The substrate was then pre-oxidized at 900°C for 10 h to produce a fine precipitation layer of alumina on the substrate, which is known to exhibit a good contact with

a γ -Al₂O₃ washcoat layer [15]. Finally, the treated substrate was rinsed with acetone. Dip-coating method was employed to deposit a γ -Al₂O₃ washcoat/FeCrAl substrate as well as to deposit a Cu-Ce and Ce-Zr mixed oxides layer on γ -Al₂O₃ washcoat/ FeCrAl substrate.

The γ -Al₂O₃ slurry was prepared by mixing 23 mass% of the Al(NO₃)₃ binder solution (Wako), 23 mass% of γ -Al₂O₃ powder, and 54 mass% of distilled water, followed by vigorous stirring (600 rpm) for 8h at room temperature to make slurry solution. After the dip-coating process, the Al₂O₃ washcoat layer was dried at room temperature for 30 min and heated at 250°C for 2 h, followed by sintering at 650°C for 2.5 h [16], where the atmospheres were ambient.

In the Cu-Ce and Ce-Zr mixed oxides deposition, the CuO-CeO₂ slurry and CeO₂-ZrO₂ slurry were prepared by mixing 23 mass% of the Al(NO₃)₃ binder solution, 23 mass% of milled CuO-CeO₂ powder and CeO₂-ZrO₂ powder and 54 mass% of distilled water, followed by high-energy ball milling (wet milling) for 30 h. The dip-coating process, drying and sintering procedure was repeated as γ -Al₂O₃ deposition.

The noble metals (Pt, Pd, Rh) supported on Cu-Ce mixed oxides, Ce-Zr mixed oxides with γ -Al₂O₃ washcoat on FeCrAl substrate and γ -Al₂O₃ washcoat on FeCrAl substrate were prepared by being impregnated with the mixed solution of Pt(NO₃)₂, Pd(NO₃)₂ and Rh(NO₃)₃ (Wako), the mole ratio of Pt:Pd:Rh = 1:14:1 (total 3.7 gram/L). The total loading amount of noble metal was wt. 4% and kept at the same weight level for Cu-Ce, Ce-Zr mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate and γ -Al₂O₃ washcoat/FeCrAl substrate respectively.

2.2. Surface Characterization

The structure and morphology of catalysts samples were analyzed by X-ray diffractometry (XRD) using Cu-K α radiation (RINGAKU RINT-2100CMT) and by scanning electron microscope (SEM, TEOL JSM-5800). The surface area was estimated by N₂ adsorption method (Brunauer-emmett-Teller). X-ray photoelectron spectroscopy (XPS) was carried out on a JEOL XPS using monochromatic Mg K α radiation.

2.3. Catalytic Activity Measurements (CO, C₃H₈, NO)

The simulant exhaust gas containing O₂, CO (1.5%), H₂ (0.5%), CO₂ (12%), C₃H₈ (0.1%), NO (0.05%) and N₂ (balance) was prepared, the λ value as oxidants/reductions factor was defined to be $\lambda = (2O_2 + NO)/(CO + H_2 + 10C_3H_8)$. The λ was adjusted by controlling the concentration of oxygen, CO, C₃H₈ and NO conversion was analyzed by GC-TCD (Varian CP-4900), the samples were put in a reaction tube (i.d = 8 mm) made from quartz. The catalytic performances were carried out at various oxygen stoichiometric operations. At stationary stoichiometric operation ($\lambda = 1$, oxygen concentration of 1.5%), the catalytic performance was measured at the reaction temperature of 30°C - 540°C, the

heating rate of 3°C/min and the gas flow of 20 ml/min. At lean/rich oxygen stoichiometric operation (oxygen concentration was changed from 2.1% to 0.42% respectively, λ value in range of 1.4 - 0.3), the catalytic performances were measured at the temperature of 500°C.

3. Results and Discussion

3.1. Textural, Structural and Morphological Characterizations

Table 1 shows the surface areas of the noble metals (Pt, Pd, Rh) support on Cu-Ce, Ce-Zr mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate and γ -Al₂O₃ washcoat/FeCrAl substrate. The surface area of 142 m²/g is demonstrated for Pt, Pd, Rh/ γ -Al₂O₃/FeCrAl substrate, surface area trends decrease due to the deposition of Cu-Ce and Ce-Zr mixed oxides on γ -Al₂O₃ washcoat, the lower surface area with the CuO content is probably due to the formation of the soft Cu phase, which may cause agglomeration of powders.

Figure 1 shows XRD patterns of the noble metals (Pt, Pd, Rh) support on Cu-Ce, Ce-Zr mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate and the noble metals (Pt, Pd, Rh) supported on γ -Al₂O₃ washcoat/FeCrAl substrate. The peaks of FeCrNi, γ -Al₂O₃ and α -Al₂O₃ are observed after pre-oxidized FeCrAl substrate at 900°C for 10 h (**Figure 1(a)**) [15], γ -Al₂O₃ peaks become sharper and the intensity of FeCrAl decrease slightly when γ -Al₂O₃ is deposited on FeCrAl substrate (**Figure 1(b)**). The reflection peak intensities of the CeO₂, CuO, ZrO₂ phase occurred after the CeO₂-CuO and ZrO₂-CeO₂ slurry is deposited on γ -Al₂O₃/FeCrAl substrate (**Figure 1(c)** and **Figure 1(d)**), no phase change of CuO, ZrO₂ and CeO₂ are observed. The XRD also shows that, no peaks of noble metals (Pt, Pd, Rh) or noble metal oxides are observed due to tiny loading of the noble metal (Pt, Pd, Rh) support on Cu-Ce, Ce-Zr mixed oxides with γ -Al₂O₃ washcoat/FeCrAl and γ -Al₂O₃ washcoat/FeCrAl substrate.

Figure 2 shows the morphology Pt, Pd, Rh/CuO-CeO₂/ γ -Al₂O₃/FeCrAl substrate. A cross-sectional SEM image of the layered catalyst is shown in **Figure 2(a)**, the particles appear often agglomerated, the fine particles of agglomerates (of size between 5 and 10 μ m) are spread on the γ -Al₂O₃ washcoat surface, those particles are interlocked with each other and the tighter the packing by bond mechanical or interfacial nature, the washcoat thickness is about 20 μ m, the **Figure 2(b)** shows surface of CuO-CeO₂/ γ -Al₂O₃/FeCrAl substrate, the higher magnification reveals a compact CuO-CeO₂ microstructure of aggregated nano-particles.

Table 1. The surface areas of the noble metals (Pt, Pd, Rh) support on Cu-Ce, Ce-Zr mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate and γ -Al₂O₃ washcoat/FeCrAl substrate.

Deposition samples	Surface area (m ² ·g ⁻¹)
Pt, Pd, Rh/ γ -Al ₂ O ₃ /FeCrAl substrate	143
Pt, Pd, Rh/CuO-CeO ₂ / γ -Al ₂ O ₃ /FeCrAl substrate	129
Pt, Pd, Rh/ZrO ₂ -CeO ₂ / γ -Al ₂ O ₃ /FeCrAl substrate	132

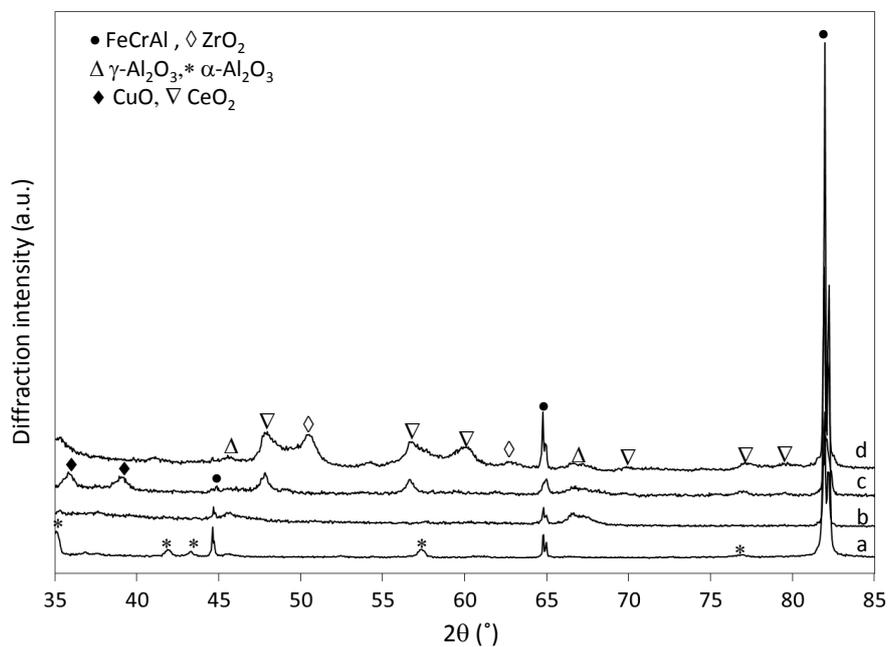


Figure 1. XRD patterns of (a) FeCrAl after pre-oxidation at 900°C for 10 h; (b) Pt, Pd, Rh/ γ -Al₂O₃ washcoat/FeCrAl; (c) Pt, Pd, Rh/CeO₂-CuO/ γ -Al₂O₃ washcoat/FeCrAl; (d) Pt, Pd, Rh/ZrO₂-CeO₂/ γ -Al₂O₃ washcoat/FeCrAl.

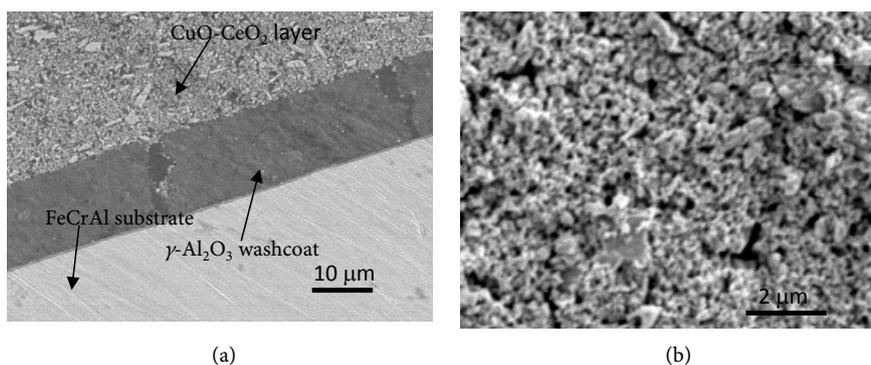


Figure 2. SEM photographs of Pt, Pd, Rh/CuO-CeO₂/ γ -Al₂O₃/FeCrAl substrate (a) interface; (b) surface.

3.2. Chemical State Analysis of Pt, Pd, Rh/CuO-CeO₂/ γ -Al₂O₃/FeCrAl Substrate

The noble metals (Pt, Pd, Rh) support on Cu-Ce mixed oxides with γ -Al₂O₃ washcoat/FeCrAl (sintered at 650°C for 2.5 h) is used for the chemical state analysis of noble metals. The **Figure 3(a)** shows Pt 4f photoelectron spectra of sample, the doublet at 71.1 and 74.2 eV are observed which may be attributed to Pt⁰ sites. The **Figure 3(b)** shows Pd 3d photoelectron spectra, the doublet at 336.1 eV and 338.1.1 eV can be attributed for Pd²⁺ and Pd⁴⁺. The **Figure 3(c)** shows Rh 3d for sample, the Rh 3p_{5/2} peaks are observed at 306.0 eV and 308.3 eV can be attributed for Rh⁰ and Rh³⁺ respectively. The results show that the chemical state of noble support on Cu-Ce mixed oxides with γ -Al₂O₃ washcoat/FeCrAl. Xiaodong Wu *et al.* [12] or S.Suhonen *et al.* [17] reported that those

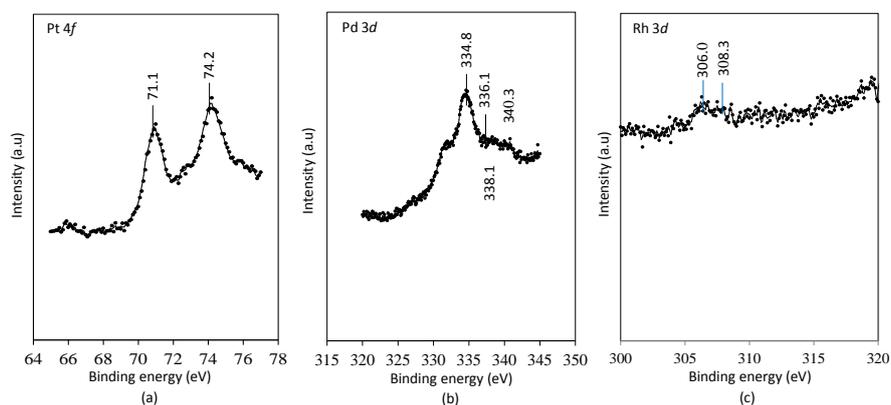


Figure 3. Photoelectron spectra of (a) Pt 4f; (b) Pd 3d and (c) Rh 3d support on CuO-CeO₂/ γ -Al₂O₃/FeCrAl substrate.

chemical states depend strongly on heated treatment condition, the noble metals oxide are observed after sintering of 650°C for 2.5 h, the reason for this may be due to the incomplete decomposition of noble metals salt.

3.3. Catalytic Performance of Samples

Figure 4 shows CO, C₃H₈, NO conversion of the noble metals (Pt, Pd, Rh) support on Cu-Ce mixed oxides with γ -Al₂O₃ washcoat/FeCrAl as a function of temperature at $\lambda = 1$. The reactions appear at the temperatures of 180°C, with the increase of temperature in range from 30°C to 540°C, the CO, C₃H₈ and NO conversion increase rapidly, the highest CO conversion of 99% is observed while C₃H₈ and NO conversion are 62% and 84.3% respectively. **Figure 5** shows comparative CO, C₃H₈, NO conversion of the noble metals (Pt, Pd, Rh) support on Cu-Ce, Ce-Zr mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate and γ -Al₂O₃ washcoat/FeCrAl substrate due to the increase of reaction temperature in range from 30°C to 540°C and at $\lambda = 1$, the highest CO conversion performance is observed for the noble metals (Pt, Pd, Rh) support on Cu-Ce with γ -Al₂O₃ washcoat/FeCrAl substrate, the result also shows that the CO oxidation reaction of the noble metals (Pt, Pd, Rh) support on Cu-Ce mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate appears at temperature of 150°C which is lower than the noble metals (Pt, Pd, Rh) support on Zr-Ce mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate and γ -Al₂O₃ washcoat/FeCrAl substrate (**Figure 5(a)**). It is reasonable to consider that the additive Cu promotes CO oxidation reaction, Meng-Fei Luo *et al.* [18] and G. Avgouropoulos *et al.* [19] are also reported that the additive Cu promotes CO oxidation reaction at low temperatures. The same trend of C₃H₈ and NO conversions are observed for the noble metals (Pt, Pd, Rh) support on Cu-Ce, Ce-Zr mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate and γ -Al₂O₃ washcoat/FeCrAl substrate (**Figure 5(b)** and **Figure 5(c)**).

Figure 6 shows comparative CO, C₃H₈, NO conversion at 500°C of the noble metals (Pt, Pd, Rh) support on Cu-Ce, Ce-Zr mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate and γ -Al₂O₃ washcoat/FeCrAl substrate at rich/lean

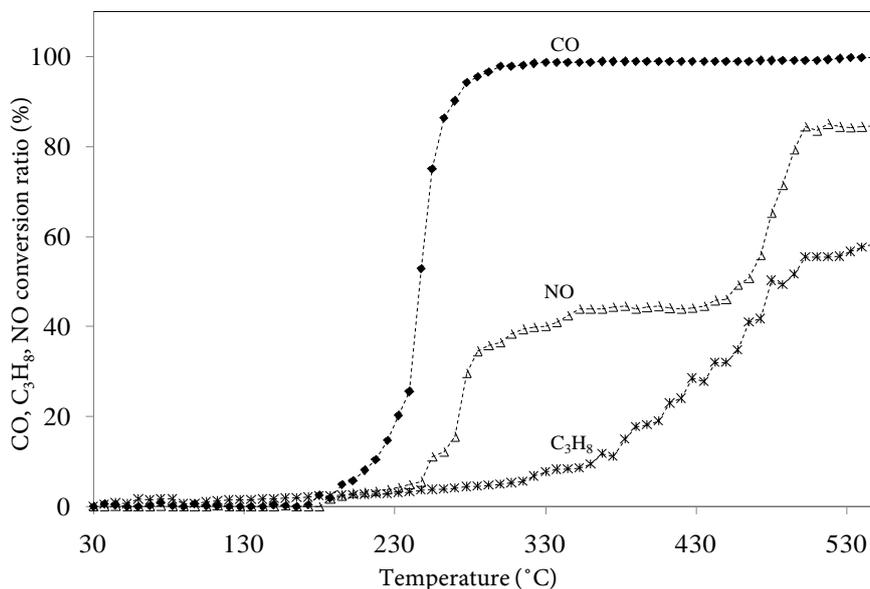
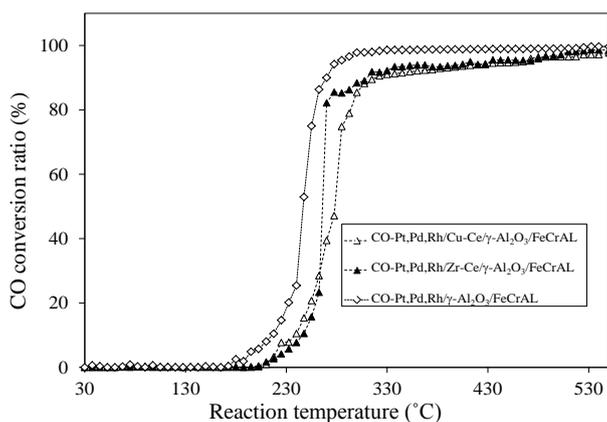
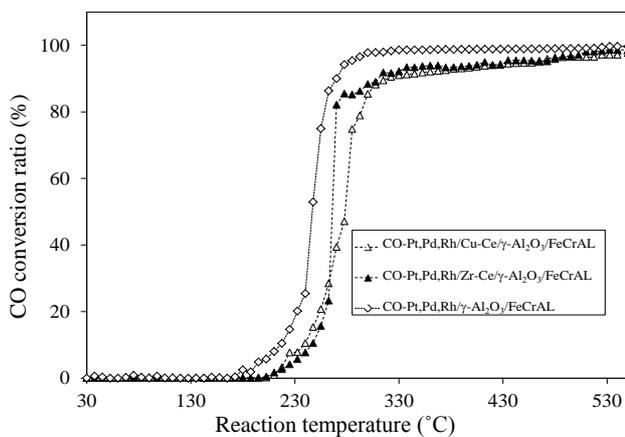


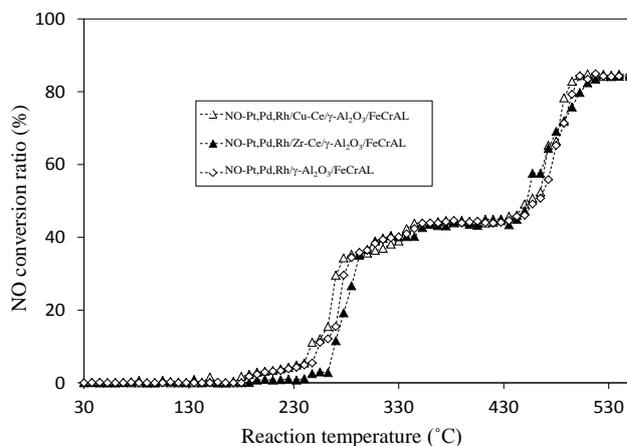
Figure 4. CO, C₃H₈, NO conversion of the noble metals (Pt, Pd, Rh) support on Cu-Ce mixed oxides with γ -Al₂O₃ washcoat/FeCrAl at $\lambda = 1$.



(a)



(b)



(c)

Figure 5. Comparative (a) CO; (b) C₃H₈; (c) NO conversion of the noble metals (Pt, Pd, Rh) support on Cu-Ce, Ce-Zr mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate and γ -Al₂O₃ washcoat/FeCrAl substrate at $\lambda = 1$.

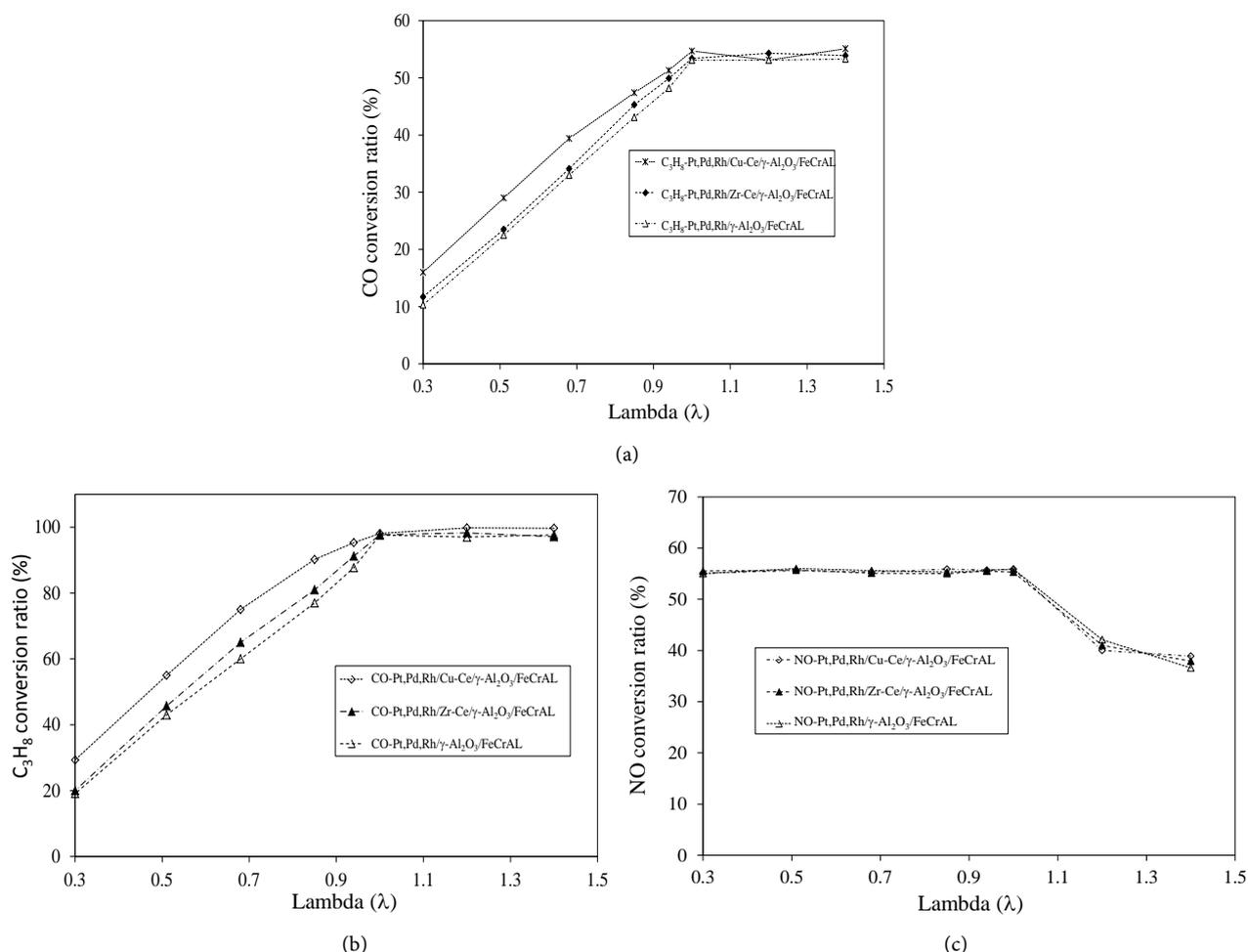


Figure 6. Comparative (a) CO; (b) C₃H₈; (c) NO conversion at 500°C of the noble metals (Pt, Pd, Rh) support on Cu-Ce, Ce-Zr mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate and γ -Al₂O₃ washcoat/FeCrAl substrate at rich/lean oxygen stoichiometric.

oxygen stoichiometric. At lean oxygen stoichiometric, CO and C₃H₈ conversion performance of the noble metals (Pt, Pd, Rh) support on Cu-Ce mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate decrease from 99.1% to 33.3% and from 55.1% to 16.2% respectively during the decrease of λ from 1 to 0.3 (**Figure 6(a)** and **Figure 6(b)**), where flat NO conversion of 55.7% is also observed (**Figure 6(c)**). Compared with CO and C₃H₈ of the noble metals (Pt, Pd, Rh) support on Zr-Ce mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate and γ -Al₂O₃ washcoat/FeCrAl substrate, those of the noble metals (Pt, Pd, Rh) support on Cu-Ce mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate is higher those of noble metals (Pt, Pd, Rh) support on Zr-Ce mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate (from 96.3% to 20% and from 53.9% to 13% respectively) and the γ -Al₂O₃ system (from 95.7% to 15.1% and from 53.3% to 10.3%). It can be suggested that the high OSC activities play an important role in the oxidation of CO and C₃H₈.

Figure 7 shows the amount of oxygen released from oxygen storage materials to support oxygen for the oxidation reaction of CO and C₃H₈, during the

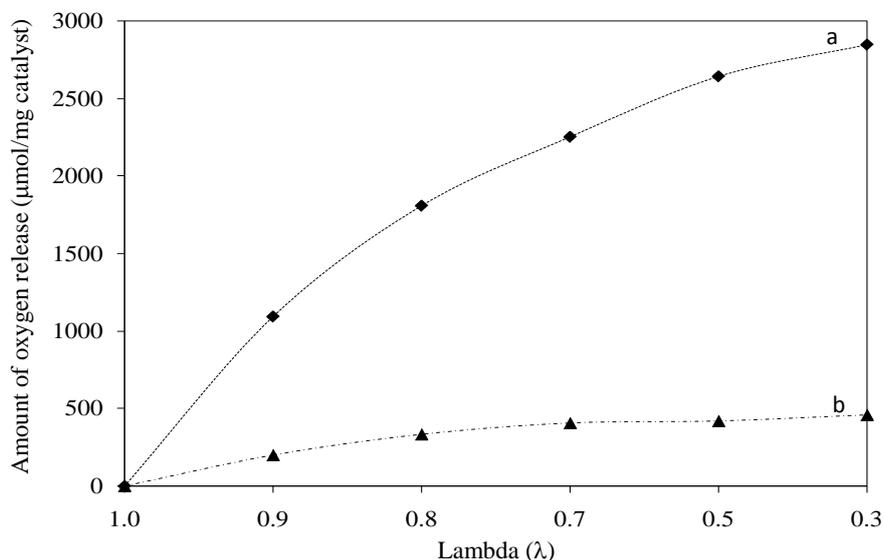


Figure 7. Oxygen release capacity at 500°C of the noble metals (Pt, Pd, Rh) support on (a) Cu-Ce and (b) Zr-Ce mixed oxides with $\gamma\text{-Al}_2\text{O}_3$ washcoat/FeCrAl substrate at lean oxygen stoichiometric.

decrease of λ values from 1 to 0.3. The amount of released oxygen is calculated based on $\gamma\text{-Al}_2\text{O}_3$ washcoat which results depict no release of oxygen. The result shows that amount of released oxygen the noble metals (Pt, Pd, Rh) support on Cu-Ce mixed oxides with $\gamma\text{-Al}_2\text{O}_3$ washcoat/FeCrAl substrate is much higher those of the noble metals (Pt, Pd, Rh) support on Zr-Ce mixed oxides with $\gamma\text{-Al}_2\text{O}_3$ washcoat/FeCrAl substrate. It has been reported [11] that a ceria-copper oxide compound (CuO-CeO_2) prepared by high energy mechanical milling to significantly promote the OSC during the valence change of Cu^{2+}/Cu and $\text{Ce}^{4+}/\text{Ce}^{3+}$. It is also quite interesting that the amount of released oxygen from oxygen storage materials is found during the decrease of λ from 1 to 0.3. It is reasonable to believe that the released oxygen may improve CO and C_3H_8 conversion at lean oxygen condition. Thus, it can improve the efficiency of TWCs.

Under an engine real working conditions, the value of λ oscillates at around 1 with a frequency of about 1 Hz [1]. Hence, the efficient conversion of TWCs decreases during the oscillation of λ . The dynamic of released oxygen from oxygen storage materials is therefore an important parameter in the improvement of the TWCs conversion efficiency. The dynamics of released oxygen was estimated for values of λ from 1 to 0.9. Result shows that, the dynamics of released oxygen of the noble metals (Pt, Pd, Rh) support on (a) Cu-Ce mixed oxides with $\gamma\text{-Al}_2\text{O}_3$ washcoat/FeCrAl substrate ($6.7 \mu\text{mol}\cdot\text{mg}^{-1}\cdot\text{s}^{-1}$) is much higher than those of the noble metals (Pt, Pd, Rh) support on Zr-Ce mixed oxides with $\gamma\text{-Al}_2\text{O}_3$ washcoat/FeCrAl substrate ($1.1 \mu\text{mol}\cdot\text{mg}^{-1}\cdot\text{s}^{-1}$).

Figure 6 also shows CO, C_3H_8 and NO conversion at rich oxygen stoichiometric (λ in range 1 - 1.4). The results show that CO and C_3H_8 conversion are flat (**Figure 6(a)** and **Figure 6(b)**) while NO conversion decreases from 55.9% to 38.9% (**Figure 6**) caused by the decrease of reduction agent. Compared the noble

metals (Pt, Pd, Rh) support on Cu-Ce, Zr-Ce mixed oxides with γ -Al₂O₃ washcoat/FeCrAl substrate and γ -Al₂O₃ washcoat/FeCrAl substrate, it shows similar CO, C₃H₈ and NO conversions during λ varies from 1 to 1.4.

4. Conclusions

Effects of CuO-CeO₂ additions on structure and catalytic Properties of Three Way Catalysts were investigated. The samples were characterized by means of XRD, SEM, Brunauer-Emmett-Teller (BET), X-ray photoelectron spectroscopy (XPS) and GC-TCD.

The catalytic performance of noble metals (Pt, Rh, Pd) supported on Cu-Ce mixed oxides with alumina washcoat was compared with noble metals (Pt, Rh, Pd) supported on Ce-Zr mixed oxides with alumina washcoat and γ -Al₂O₃ washcoat at various stoichiometric ratio of oxygen. The results showed that the addition of Cu-Ce mixed oxides improved CO oxidation reaction at lower temperature during stable lambda of 1, the highest CO conversion of 99% is observed for the noble metals (Pt, Pd, Rh) support on Cu-Ce with γ -Al₂O₃ washcoat/FeCrAl substrate. The results also showed that, the addition of Cu-Ce mixed oxides promoted released oxygen, thus it improved strongly CO and C₃H₈ conversion at lean oxygen stoichiometric operation.

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