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Article

Catalytic performance of Pt–Rh/CeZrYLa+LaAl with stoichiometric natural gas vehicles emissions

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ABSTRACT

The composite support CeZrYLa+LaAl was prepared by a co-precipitation method, and Pt–Rh bimetallic catalysts were fabricated on this support using different preparation procedures. The catalytic activities of these materials were tested in a gas mixture simulating the exhaust from a stoichiometric natural gas vehicle. The as-prepared catalysts were also characterized by X-ray photoelectron spectroscopy, X-ray diffraction, N₂ adsorption-desorption and H₂-temperature-programmed reduction. It was found that the order of activities for CH₄, CO and NO conversion was Cat3 > Cat2 > Cat1, where Cat3 had the lowest light-off temperature (T_{50}) for CO (114 °C) and NO (149 °C), the lowest complete conversion temperature (T_{90}) for CH₄ (398 °C) and CO (179 °C), and the lowest ΔT ($T_{90}-T_{50}$) for CH₄ (34 °C) and CO (65 °C). Cat2 showed the lowest T_{50} for CH₄ (342 °C), the lowest T_{90} for NO (174 °C), and the lowest ΔT for NO (17 °C). Cat1 had the highest T_{50} and T_{90} and the largest ΔT out of all three catalysts. Indicating that Pt–Rh bimetallic catalysts (Cat2 and Cat3) prepared by physically mixing Pt and Rh powders exhibited much better catalytic activity than those (Cat1) prepared by co-impregnation, since homogeneous Pt and Rh sites made a significant contribution to CH₄/CO/NO conversions. In contrast, strong Pt–Rh interactions in the co-impregnation materials affected the oxidation states of Pt, and the Pt-enriched surface blocked active Rh sites. Moreover, Cat3 was prepared by adding additives (La³⁺, Zr⁴⁺ and Ba²⁺) into the physically mixed Pt–Rh catalysts. XRD results demonstrated that the additive cation (Zr⁴⁺) was incorporated into the CeO₂–ZrO₂ lattice, thus creating a higher concentration of defects and improving the O₂-mobility. XPS results showed that the Cat3 had the highest Ce³⁺/Ce ratio, suggesting the presence of a significant quantity of oxygen vacancies and cerium in the Ce³⁺ state. All of these further promoted the three-way catalytic activity and widened the air-to-fuel working-window.

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1. Introduction

There are presently more than 16.7 million natural gas ve-

hicles (NGVs) operating globally. Recognized as the cleanest hydrocarbon fuel, compressed natural gas (CNG) is less expensive than gasoline and produces lower quantities of CO₂, nitric

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oxide and other pollutants than gasoline or diesel. CNG thus has the potential to reduce some of the problems associated with environmental pollution and scarce oil resources. Furthermore, CH₄ (which constitutes about 90% of natural gas by volume) has the highest proportion of hydrogen in any fossil fuel, and its use thus reduces CO₂ emissions per megajoule, compared with other fuels [1]. CH₄ itself, however, is a much more potent greenhouse gas than CO₂ and unburned CH₄ is the major hydrocarbon component of exhaust from NGVs [2] and so it is necessary to use a catalytic converter to eliminate CH₄ from the exhaust stream.

NGV engines typically operate as stoichiometric or lean burn combustion systems and, in stoichiometric systems, NO_x, CO and unburned CH₄ are the main harmful pollutants. Current emission controls used in NGVs primarily use the same three-way catalysts employed in gasoline vehicles, but with a higher noble metal content. The catalyst support is normally alumina owing to its high surface area, good thermal stability and low cost [3]. However, commercial stoichiometric NGV catalysts operate in a narrow equivalence ratio window, requiring a high capacity oxygen storage material. Recently, oxygen storage materials such as ceria–zirconia have been employed to improve the mobility and diffusion of bulk oxygen to obtain more efficient stoichiometric NGV catalysts. Bounechada *et al.* [1] investigated a Ce–Zr-promoted Pd–Rh/Al₂O₃ catalyst for the reduction of CH₄ in NGV exhaust under both stoichiometric and periodic lean–rich switching conditions, while Klingstedt *et al.* [4] studied a Pd–Ce-supported alumina catalyst intended for the post-combustion of emissions from NGVs. Stoichiometric NGV catalysts are commonly operated at high exhaust gas temperatures and so the use of rare-earth metals to improve the thermal stability of supports [5], such as CeO₂–ZrO₂–La₂O₃–PrO₂–Al₂O₃ and CeO₂–ZrO₂–M_xO_y (M = Y, La)/Al₂O₃ composites supports, has been widely applied [6,7]. The present work examines a CeZrYLa+LaAl composite oxide that combines the advantages of both Al₂O₃ and CeO₂–ZrO₂ was prepared by a co-precipitation method and investigated as a catalytic support.

Generally, noble metal catalysts such as Pt, Pd and Rh play a key role in NGV catalysts. Oh *et al.* [8] suggested that Pd was predominantly used under lean-burn condition due to its high activity in CH₄ oxidation. Pt catalysts have been found to be superior to Pd under rich-burn conditions [9]. Rh exhibits high efficiency for reducing nitrogen oxides [10] and promotes the catalytic destruction of C₃H₈ and inhibits sintering of PdO_x [11]. In past work by our group, Pd catalysts used for lean-burn NGVs were studied [12–14], employing the same CeO₂ and/or La₂O₃-modified Pd/YZ–Al₂O₃ catalysts use for stoichiometric NGVs [15]. Yuan *et al.* [16] designed medium-coupled Pt–Rh monolithic catalysts for NGVs that were capable of meeting Euro III emission requirements. In addition, methods of loading noble metals have been studied extensively. Pt–Rh/Al₂O₃ has been prepared by the co-impregnation method [17], while Hu *et al.* [10] reported an alternative method for the synthesis of Pt–Rh three-way catalysts by physically mixing Pt and Rh. The effects of the preparation methods used to fabricate the precious metals on catalytic activity have been less studied. Oxide

additives also improve the catalytic activity, and La³⁺ ions have been shown to improve the dispersion of active sites, thus increasing catalytic activity [18,19]. ZrO₂ has attracted considerable attention because of its thermal stability, acidity, and alkaline and redox properties. The addition of BaO was also found to promote the catalytic oxidation of propene over Pt/Al₂O₃ [20].

In the present study, the nanocomposite support CeZrYLa+LaAl functioned as a carrier. Pt–Rh bimetallic catalysts were prepared by physically mixing Pt and Rh catalyst powders and by using a co-impregnation method to study the effects of preparation methods on catalytic activity. Additionally, a physically mixed Pt–Rh catalyst with added La³⁺, Zr⁴⁺ and Ba²⁺ was also investigated.

2. Experimental

2.1. Support preparation

The composite oxide CeO₂–ZrO₂–Y₂O₃–La₂O₃ + La₂O₃–Al₂O₃ (CeZrYLa+LaAl) was obtained by precipitating the Ce(NO₃)₃·6H₂O, ZrOCO₃, La(NO₃)₃·6H₂O, and Y(NO₃)₃·6H₂O mixed solution and La(NO₃)₃·6H₂O and Al(NO₃)₃·9H₂O mixed solution with NH₃·H₂O precipitator, respectively. And then the precursor of Y³⁺ and La³⁺-modified ceria–zirconia and La³⁺-modified alumina were mixed together with intense stirring. The precipitate was filtered, washed, dried and then calcined at 800 °C for 3 h in a muffle furnace to obtain the support. The resulting CeZrYLa+LaAl composite oxide had a CeZrYLa/LaAl mass ratio of 7:3 and Ce/Zr/Y/La and La/Al mass ratios of 45:45:5:5 and 3:97.

2.2. Catalyst preparation

Using the support prepared above as a carrier, Pt–Rh catalysts were synthesized using different preparation methods. The sample termed Cat1 was prepared using a conventional co-impregnation method. In this method, mixed aqueous solutions of Pt(NO₃)₂ and Rh(NO₃)₃ were co-impregnated on the support powder, which was then dried overnight at 120 °C. Cat2 was obtained by impregnating a quantity of the support with Pt(NO₃)₂ and a second quantity with Rh(NO₃)₃. After drying at 120 °C overnight, the two portions were mixed together. Cat3 was prepared in the same manner as Cat2 except adding 3.7 wt% La³⁺, 6.3 wt% Zr⁴⁺ and 3.7 wt% Ba²⁺ to the mixed powder. The Pt and Rh loadings in each catalyst support were 1.28 and 0.14 wt%, respectively. Each of the prepared powder catalysts was calcined at 550 °C for 3 h and ball-milled with the appropriate amount of deionized water to obtain a homogeneous slurry, following which the resulting slurry was coated onto honeycomb cordierite (length: 2.5 cm, volume: 2.7 cm³, Corning). The coated catalysts were dried overnight at 120 °C and calcined at 550 °C in air for 3 h to obtain the monolithic catalysts. The catalyst loading were approximately 150 g L⁻¹ and the Pt–Rh loading was 2.14 g L⁻¹ (60 g/ft³) with a 9:1 mass ratio.

2.3. Support and catalyst characterization

The textural properties of the supports were assessed by N₂ adsorption-desorption at −196 °C, using an automated surface area and pore size analyzer (Autosorb SI, Quantachrome, USA). Samples were pretreated at 300 °C for 5 h prior to these analyses. Surface areas were determined using the BET model.

Powder X-ray diffraction (XRD) data were acquired on a Japan Science D/max-RA diffractometer using Cu K α (λ = 0.15406 nm) radiation. The tube voltage and current were 40 kV and 100 mA, respectively and patterns were acquired over the range of 10°–80°.

X-ray photoelectron spectroscopy (XPS) data were obtained using a Kratos XSAM-800 spectrophotometer operating at 13 kV and 20 mA with Al K α radiation (1486.6 eV) in the constant pass energy mode (20 eV pass energy). The C 1s peak at 284.8 eV was used for calibration of binding energy (BE) values. The pressure in the analytical chamber was approximately 10^{−9} Pa.

Hydrogen temperature-programmed reduction (H₂-TPR) analyses were performed using instrumentation made in-house and incorporating a thermal conductivity detector. Samples of 100 mg were pretreated in a quartz tubular micro-reactor under a flow of pure N₂ at 450 °C for 1 h to ensure clean surfaces and then cooled to room temperature. Reduction was carried out under a flow of 5% H₂/N₂ between room temperature and 900 °C at a heating rate of 8 °C/min.

2.4. Catalyst activity testing

Catalytic activity test was performed in a multiple fixed bed continuous flow micro-reactor using a gas mixture simulating the exhaust from a NGV operating under stoichiometric condition. Trials were performed from 100 to 500 °C. The simulated exhaust was composed of CH₄ (0.087 vol%), CO (0.40 vol%), NO (0.073 vol%), H₂O (10–12 gas/vol%) and CO₂ (12 vol%), with N₂ as the balance. The O₂ content was adjusted to obtain a stoichiometric mixture. The gas hourly space velocity (GHSV) was 34000 h^{−1}. The gases were regulated using mass-flow controllers before entering the reactor. The air–fuel ratio window, defined as the ratio between available oxygen and oxygen required for the conversion of CH₄, CO and NO, was assessed at

500 °C. The concentration of CH₄ was analyzed by an online gas chromatograph equipped with a flame ionization detector (FID), while CO and NO were determined online using a five-component analyzer FGA-4100 (Fofen Analytical Instrument Co., Ltd., Foshan, China) before and after the simulated exhaust gas passed through the reactor. The conversions of CH₄, CO, and NO were calculated using the following formula:

$$\text{Conversion} = ((C_{\text{in}} - C_{\text{out}}) / C_{\text{in}}) \times 100\% \quad (1)$$

Here C_{in} is the component concentration in the original simulated exhaust mixture prior to the micro-reactor, and C_{out} is the concentration after the micro-reactor.

3. Results and discussion

3.1. N₂ physisorption and XRD results

The BET specific surface area, pore volume, and pore size of CeZrYLa+LaAl sample calcined at 800 °C are 148.2 m²/g, 0.40 ml/g, and 5.05 nm, respectively.

Fig. 1 shows the XRD patterns of the support and catalysts. The main diffraction peaks of all samples were consistent with the characteristic peaks of tetragonal Ce_{0.5}Zr_{0.5}O₂ (PDF-ICDD38-1436). These results are also in good agreement with the reported by ones [21,22], in which tetragonal phases were formed in the 5 to 60 mol% CeO₂ composition range. Diffraction peaks corresponding to CeO₂ and ZrO₂ were not detected, suggesting that the Ce and Zr were primarily present as CeO₂–ZrO₂ mixed oxides. The patterns do not contain any γ -Al₂O₃ peaks, and the absence of characteristic Al₂O₃ peaks indicates that the Al₂O₃ was either incorporated into the CeO₂–ZrO₂ lattice to form a solid solution or formed grains that were too small to be detected by XRD [23]. Pt and Rh phases were not observed, indicating that the noble metals were well dispersed on the support or that the Pt and Rh concentrations were too low to be detected. Furthermore, a peak attributed to monoclinic ZrO₂ (2θ = 24.2°) was present in the pattern of the Cat3 sample because of the addition of 6.3 wt% ZrO₂.

The main (101) diffraction peaks appear between 26° and 33° and this region has been enlarged and is presented as Fig. 1(b). The associated crystallite sizes (calculated based on Bragg's law: $2d\sin\theta = k\lambda$) and other parameters are summa-

Fig. 1. (a) XRD patterns of support and catalysts; (b) XRD patterns in the 2θ range from 26° to 33°.

rized in Table 1. The peak at 29.32° was assigned to the (101) planes of tetragonal $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$. The peak intensities of the Cat1 and Cat2 are slightly reduced compared with the support. In contrast, the peak intensities of the Cat3 sample are significantly reduced, demonstrating that the additive cations (La^{3+} , Zr^{4+} , Ba^{2+} and especially Zr^{4+}) were incorporated into the CeO_2 – ZrO_2 lattice, thus increasing its structural defects and reducing the degree of crystallinity. Moreover, the Cat1 and Cat2 peaks were shifted to slightly higher 2θ values, while the Cat3 exhibited a more pronounced shift from 29.32° to 29.56° . These results are in good agreement with the observed decreases in the lattice parameters (Table 1). The ionic radii of Pt^{2+} , Pt^{4+} , and Rh^{3+} are 0.080, 0.063 and 0.0665 nm, all of which are smaller than those of Ce^{4+} (0.097 nm) and Zr^{4+} (0.084 nm). Thus, a decrease in the lattice parameters indicates that a small quantity of Pt^{2+} , Pt^{4+} , or Rh^{3+} ions have possibly dissolved in the CeO_2 – ZrO_2 lattice. The decrease in the lattice parameters in the case of Cat3 was greater than for the Cat1 and Cat2 because of the addition of Zr^{4+} (6.3 wt%), since the ionic radius of Zr^{4+} (0.084 nm) is smaller than that of Ce^{4+} (0.097 nm) [24,25]. On the contrary, lower concentrations of La^{3+} and Ba^{2+} were added compared with the Zr^{4+} loading, but these ions have larger ionic radii than Ce^{4+} and Zr^{4+} (0.103 and 0.135 nm, respectively), indicating that the La^{3+} and Ba^{2+} barely dissolved in the CeO_2 – ZrO_2 lattice and instead may have been well dispersed over the support. The XRD results demonstrate that the insertion of noble metals and the additive Zr^{4+} into the ceria lattice created a higher concentration of defects, improving the O_2 mobility [24,26].

3.2. XPS results

XPS analyses were performed to verify the surface compositions and elemental oxidation states. The Ce 3d XPS spectra obtained from the support and catalysts are presented in Fig. 2, while Table 2 provides the BEs of the characteristic peaks for Ce atoms and the Ce^{3+}/Ce ratios for all samples. In Fig. 2, the Ce 3d peaks are seen to be complex, consisting of eight components denoted as u or v. Here the u series represents the $\text{Ce}^{3+} 3d_{3/2}$ contribution while the v series represents the $\text{Ce}^{4+} 3d_{5/2}$ contribution. The labels u, u2, and u3 were assigned to the $\text{Ce}^{4+} 3d_{3/2}$ peaks and the v, v2 and v3 labels were assigned to the $\text{Ce}^{4+} 3d_{5/2}$ peaks [27]. The Ce^{3+} signal generated only two peaks, labeled u1 and v1, because of the $3d^{10}4f^1$ orbital. In all samples, the peak intensities assigned to Ce^{4+} were evidently stronger than those arising from Ce^{3+} , demonstrating that Ce^{4+} was the primary chemical state. Table 2 shows that Cat1 had the lowest $\text{Ce}^{4+} 3d_{3/2}$ (u) and $\text{Ce}^{4+} 3d_{5/2}$ (v) BE values of 900.62 and 882.37 eV, indicating that the electron cloud densities associated with

Fig. 2. XPS spectra showing Ce 3d peaks for the support and catalysts.

Table 2

The binding energies of the characteristic peaks of Ce atoms and Ce^{3+}/Ce ratios.

Sample	Binding energy (eV)				Ce^{3+}/Ce (%)
	$\text{Ce}^{3+} 3d_{3/2}$ (u1)	$\text{Ce}^{4+} 3d_{3/2}$ (u)	$\text{Ce}^{3+} 3d_{5/2}$ (v1)	$\text{Ce}^{4+} 3d_{5/2}$ (v)	
Support	904.21	900.93	885.60	882.23	10.76
Cat1	904.24	900.62	886.10	882.37	10.68
Cat2	904.52	900.80	885.35	882.43	10.93
Cat3	903.39	901.05	885.20	882.48	15.94

$\text{Ce}^{4+} 3d_{3/2}$ (u) and $\text{Ce}^{4+} 3d_{5/2}$ (v) were lower in Cat2 and Cat3, such that the Ce^{4+} ions were more readily reduced to Ce^{3+} . In the case of the $\text{Ce}^{3+} 3d_{3/2}$ (u1) and $\text{Ce}^{3+} 3d_{5/2}$ (v1) values, Cat3 had the lowest BE values of 903.39 and 885.20 eV, respectively, indicating that the $\text{Ce}^{3+} 3d_{3/2}$ and $\text{Ce}^{3+} 3d_{5/2}$ electron cloud densities were the highest in this sample, thus the Ce^{3+} more readily lost electrons to oxidize to Ce^{4+} [28,29], increasing the mobility of active oxygen between Ce^{3+} and Ce^{4+} . This reaction may have proceeded according to the following equation:

The Ce^{3+}/Ce ratios in these samples were determined by dividing the sum of the areas of the Ce^{3+} peaks by the sum of the areas of all cerium peaks, and the results are given in Table 2. These data show that the Cat3 had the highest Ce^{3+}/Ce ratio, suggesting the presence of a significant quantity of oxygen vacancies and Ce in the Ce^{3+} state. The low valence state of the Ce species, as well as a high concentration of oxygen vacancies and a charge imbalance on the catalyst surface, which favors the redox transformation between Ce^{3+} and Ce^{4+} , all work to increase both oxygen activation and mobility. From these results, it is evident that the addition of Zr^{4+} to the ceria–zirconia solid solutions created both a charge imbalance and defects on the catalyst surface, promoting the formation of oxygen vacancies and increasing the mobility of active oxygen between Ce^{3+} and Ce^{4+} . These findings are in agreement both with the present XRD results and with data presented in the literature [30].

The surface atomic concentrations of Ce, Zr, Al, O, La, and Ba are summarized in Table 3. These data show that the absolute percentages of Ce, Zr, Al, La, and O were slightly decreased in the Cat1 and Cat2 samples compared with the original support, since the Pt and Rh species would have occupied some surface

Table 1

Lattice parameter and crystallite sizes as determined by XRD.

Sample	Main phase composition	Cell parameters		Crystallite size (nm)
		a (nm)	c (nm)	
Support	Tetragonal $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	0.37360	0.53090	5.1
Cat1	Tetragonal $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	0.37222	0.52968	4.8
Cat2	Tetragonal $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	0.37255	0.53044	4.9
Cat3	Tetragonal $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	0.37086	0.52913	4.8

Table 3

Surface elemental compositions and atomic ratios of the support and catalysts as determined by XPS.

Sample	Surface atomic concentration (%)					
	Ce	Zr	Al	O	La	Ba
Support	4.54	6.72	28.02	59.61	1.11	—
Cat1	2.73	5.19	30.29	59.21	0.91	—
Cat2	3.35	5.87	29.35	58.69	1.06	—
Cat3	2.49	6.92	28.84	58.20	1.14	1.18

sites. In addition, the Zr, La, and Ba concentrations in the Cat3 increased very little in comparison with those in the support; the loading of La^{3+} , Zr^{4+} , and Ba^{2+} into Cat3, which occupied some surface sites, led to only slight decreases in the atomic percentages of Ce and O. These results agree with the Ce 3d peaks intensities obtained for the catalysts as presented in Fig. 2.

Rh was not detected owing to its low concentrations in the prepared samples. To further study the chemical states of Pt and Rh in these catalysts, the concentration of Rh was increased in newly prepared Pt, Rh and Pt–Rh bimetallic catalysts, using the same synthesis procedure noted above. The Pt and Rh catalysts were prepared by impregnation method (2 wt% Pt and 2 wt% Rh, labeled as Pt and Rh, respectively). The bimetallic Pt–Rh catalysts (1 wt% Pt and 1 wt% Rh) were prepared using the same co-impregnation procedure employed to produce Cat1 (labeled as C–Pt+Rh) and by physically mixing Pt and Rh catalyst powders in the same manner as for Cat2 (labeled as M–Pt+Rh). The Rh 3d and Pt 4d_{5/2} peaks are shown in Fig. 3. A comparison of the spectra of M–Pt+Rh and C–Pt+Rh with the linear superposition spectra of Pt and Rh (Fig. 3) shows that the M–Pt+Rh spectrum is completely coincident with the linear superposition spectra of Pt and Rh, while the Pt 4d_{5/2} peak for C–Pt+Rh is increased to 316.40 eV. These results indicate that the bimetallic Pt–Rh catalyst prepared by physically mixing Pt and Rh monometallic catalysts had a catalyst surface structure equivalent to a homogeneous mixture of Pt and Rh sites. On the contrary, there was a strong interaction between Pt and Rh in the material produced by co-impregnation, as shown by the Pt 4d_{5/2} transition.

Furthermore, as is evident from Fig. 3, all samples exhibited

Fig. 3. XPS spectra of Rh 3d and Pt 4d_{5/2} peaks. Pt and Rh (a) and M–Pt+Rh and C–Pt+Rh (b) compared with the linear superposition spectrum of Pt and Rh. Solid and dotted lines represent data from the catalyst and the linear superposition spectra of Pt and Rh.

Fig. 4. Peak fitting of the Rh 3d, Y 3p_{1/2} and Pt 4d_{5/2} XPS spectra of the M–Pt+Rh and C–Pt+Rh samples.

peaks around 312.12 eV, attributed to Y 3p_{1/2}. Peaks at 309.50 eV due to Rh 3d_{5/2} and 315.20 eV due to Pt 4d_{5/2} are seen in the case of the M–Pt+Rh sample, whereas the Pt 4d_{5/2} peak is shifted to 316.4 eV for the C–Pt+Rh sample. In the C–Pt+Rh and M–Pt+Rh catalyst spectra, the Rh 3d, Pt 4d_{5/2} and Y 3p_{1/2} peaks overlap, although the individual peaks can be obtained by peak fitting. From this fitting procedure, the peak positions and relative areas as well as the distance between the Rh 3d_{5/2} and Rh 3d_{3/2} peaks can be determined, and the results are presented in Fig. 4. Here the Rh 3d_{5/2} and Rh 3d_{3/2} BE values for C–Pt+Rh and M–Pt+Rh are seen to be 309.50 and 314.30 eV. The Y 3p_{1/2} peaks of the two samples remain at the same position of about 312.12 eV. For the M–Pt+Rh catalyst, the Pt 4d_{5/2} peak appears at 315.20 eV, while the same peak for C–Pt+Rh is shifted to 316.40 eV, in agreement with the results shown in Fig. 3. The surface Rh/(Rh+Pt) and Pt/(Rh+Pt) atomic ratios were calculated and are found in Table 4. The results show that the Pt/(Rh+Pt) value for C–Pt+Rh was higher than that for M–Pt+Rh, possibly because the co-impregnation sample surface was enriched in terms Pt, which blocked some Rh active sites even though the initial concentration ratio of Pt to Rh was 1:1. It is worth noting that the Pt–Rh active sites in M–Pt+Rh were not chemically activated and that the Pt and Rh exhibited

Table 4

Surface atomic ratios of noble metals for the C–Pt+Rh and M–Pt+Rh samples.

Sample	Surface atomic ratios (%)	
	Rh/(Rh+Pt)	Pt/(Rh+Pt)
C–Pt+Rh	0.15	0.85
M–Pt+Rh	0.25	0.75

close-coupled physical contact. Both Pt and Rh were thus active components in the catalyst. However, there was a strong interaction between Pt and Rh in the C–Pt+Rh, and so Pt likely migrated to the catalyst surface and blocked some Rh sites.

3.3. H_2 -TPR results

The redox properties of all samples were determined by H_2 -TPR and the results are summarized in Fig. 5. The support presented a main peak at 595 °C with a shoulder at the low temperature side, attributed to the reduction of the ceria–zirconia solid solution. The TPR profiles of pure CeO_2 typically show two peaks at about 500 and 850 °C, attributed to surface and bulk reduction, respectively [31]. In this work, the TPR profile of the composite oxide exhibited a single, broad main peak between 385 and 660 °C. This was the result of the increased mobility of bulk oxygen in ceria–zirconia solid solutions after the introduction of Zr^{4+} into the ceria lattice. This result was in good agreement with previous reports [32,33].

The TPR profiles of the Pt–Rh/CeZrYLa+LA catalysts were obviously different from that of the support. The peak (α) below 200 °C was dominant for each of the catalysts, while the peaks (β and γ) at approximately 240 and 400 °C were weak. As reported in the Ref. [34], all Pt species can be reduced to Pt metal below 500 °C, with the main reduction peak appearing at 180 °C. The reduction of Rh and Pt is seen below 200 °C, especially in the case of Rh which appears on the lower temperature side [7]. It is evident that the peak area ratio (α/β) was far greater than the Rh/Pt (1:9) ratio of the as-prepared catalyst, suggesting that the first peak (α) was because of the reduction of Rh species, and to the reduction of overlapped Pt and Rh species, as well as surface and some subsurface Ce^{4+} species. This resulted from the addition of noble metals that effectively

promoted the reduction ability of the ceria–zirconia support, activating H_2 and then spilling it over onto the support [30]. The second peaks (β) can be assigned to the presence of small Pt particles strongly interacting with the support. The third peaks (γ) were very weak at about 400 °C, because of the removal of oxygen from a small proportion of the unpromoted subsurface ceria–zirconia powders. As shown in Fig. 5, the order of the reduction temperatures of α and β peaks was Cat3 < Cat2 < Cat1. The catalysts generated by physically mixing Pt and Rh showed better reducibility than the catalyst co-impregnated with Pt and Rh. This difference may result from the interaction between Pt and Rh during co-impregnation, which modifies the nature of the active surface. The XPS results above demonstrate that there was significant interaction between the Pt and Rh in the co-impregnation Pt–Rh catalyst, and that the catalyst surface was enriched in Pt which, in turn, blocked some Rh sites. It has been reported [35] that Pt enriched-bimetallic Pt–Rh particles exhibit large particle sizes and a high reduction temperature. The profile of the additive-promoted Cat3 showed the lowest reduction temperature, indicating that the addition of the additives La^{3+} , Ba^{2+} and Zr^{4+} was able to facilitate the reduction of precious metals species. This could have occurred because these additives dispersed the precious metals to form a discontinuous phase, perhaps reducing the interaction between the noble metals and the support.

3.4. Catalytic activity

The catalytic activities for CH_4 and CO oxidation and NO reduction over all catalysts under a simulated exhaust gas with a GHSV of 34000 h^{-1} are depicted in Fig. 6. It is evident that the order of activities for CH_4 , CO, and NO conversion was Cat3 $\approx$ Cat2 > Cat1. The conversions of CH_4 and CO are also seen to have increased continuously with temperature, while the NO conversions over Cat2 and Cat3 increased as temperature increased but varied in an irregular manner over Cat1. In the range from 150 to 390 °C, CH_4 did not react, while the NO reactivity initially increased before plateauing at about 250 °C and then decreasing with further increases in temperature. Because the CH_4 did not react, the NO only reacted with the CO. In the range from 390 to 500 °C, the NO conversion coincided with the CH_4 conversion and increased rapidly with increased temperature. It has been reported [15] that NO conversion can be controlled via its reaction with CO at low temperatures but proceeds by reaction with CH_4 at high temperatures, which is in agreement with our results. The main reactions associated with this process are as follows:

In the case of Cat1, Reactions (3) and (4) are predominant from 150 to 250 °C. When the temperature increases from 250 to 390 °C, the $CO + O_2$ reaction (Reaction 3) proceeds more quickly than the $NO + CO$ reaction (Reaction 4), leading to a decrease in the NO conversion over Cat1 in this range. With further increases in temperature, CH_4 takes part in the reaction and NO

Fig. 5. H_2 -TPR profiles of support and catalysts.

Fig. 6. Conversions of CH₄ (a), CO (b), and NO (c) as functions of temperature over different catalysts.

conversion proceeds via Reaction (6) and increases rapidly in the range from 390 to 500 °C. NO conversions over Cat2 and Cat3 were superior to that over Cat1, possibly because of Pt enrichment of the Pt–Rh active sites on Cat1, blocking the high efficiency of Rh for the reduction of NO. The XPS results might also be relevant here, in which Cat3 and Cat2 showed greater quantities of oxygen vacancies and Ce³⁺, as well as a higher mobility of active oxygen between Ce³⁺ and Ce⁴⁺ than Cat1. Thus, the conversion of NO benefited from the Ce³⁺/Ce⁴⁺ redox pair and was also related to the stability of the surface oxygen vacancies [36], such that the NO conversion occurred at the expense of the Ce³⁺/Ce⁴⁺ redox couple. Furthermore, both CH₄ and CO conversion over Cat2 and Cat3 were higher than over Cat1. Therefore, the catalytic activity of the catalyst made by physically mixing Pt and Rh was superior to that of the catalyst co-impregnated with Pt and Rh.

T_{50} , T_{90} , and ΔT ($T_{90}-T_{50}$) data are presented in Table 5. Here, the light-off temperature (T_{50}) and complete conversion temperature (T_{90}) are the temperatures at which the conversion of a given pollutant reached 50% and 90%, respectively, and ΔT is the temperature range between T_{50} to T_{90} . Generally, T_{50} and T_{90} are used to evaluate the catalytic activity during exhaust gas purification. It can be seen that Cat3 had the lowest T_{50} for CO (114 °C) and NO (149 °C), and the lowest T_{90} for CH₄ (398 °C) and CO (179 °C). The ΔT values for Cat3 were 34 °C for CH₄ and 65 °C for CO; these values were much smaller than

Table 5

Light-off temperatures and complete conversion temperatures for CH₄, NO and CO conversion over different catalysts.

Sample	T_{50} (°C)			T_{90} (°C)			ΔT ($T_{90}-T_{50}$) (°C)		
	CH ₄	CO	NO	CH ₄	CO	NO	CH ₄	CO	NO
Cat1	440	153	414	>500	361	451	>60	208	37
Cat2	342	117	157	405	269	174	63	152	17
Cat3	364	114	149	398	179	192	34	65	43

those of Cat2 and Cat1. The small ΔT values suggest that each pollutant reached complete conversion almost immediately after light-off, indicating that the catalyst exhibited remarkable temperature properties. Cat2 showed the lowest T_{50} for CH₄, the lowest T_{90} for NO and the lowest ΔT for NO, while exhibiting slightly lower catalytic activity than Cat3. Cat1 had the highest T_{50} and T_{90} and the largest ΔT out of all three catalysts.

CH₄, CO and NO conversions over the three catalysts at 500 °C under different O₂ concentrations are illustrated in Fig. 7. For each catalyst, all three pollutants showed the best conversion at an O₂ level near 0.22 vol%. Under oxygen-poor condition (O₂ < 0.22%), NO could be 100% converted using Cat2 and Cat3, with above 94% conversion for Cat1. CH₄ conversions were between 76% and 86% for Cat1, 67% to 92% for Cat2 and reached 100% for Cat3 under oxygen-poor condition. Cat3 showed excellent activity for CH₄ and NO conversions under rich burning conditions because of its higher concentration of oxygen vacancies and Ce³⁺/Ce⁴⁺ redox pairs [36]. Under oxy-

Fig. 7. Variations of the CH₄, CO, and NO conversions with the O₂ concentration over different catalysts at 500 °C. (a) Cat1; (b) Cat2; (c) Cat3.

gen-rich conditions ($O_2 > 0.22\%$), NO conversions over all catalysts rapidly decreased with increases in the O_2 concentration. The CH_4 conversions over Cat1 and Cat2 followed the same trend as the NO conversion, while the CH_4 conversion over Cat3 decreased slightly, indicating that the CH_4 conversion over Cat3 was higher than over Cat1 or Cat2. In each O_2 working-window, CO conversions over all catalysts increased as the O_2 concentration increased, and Cat3 exhibited the highest CO conversion.

From the above discussion, it can be concluded that the catalytic activity and working-window of Cat3 were superior to those of the other catalysts. In the case of those catalysts made by physically mixing Pt and Rh (Cat2 and Cat3), thus preventing the generation of Pt-enriched large bimetallic Pt–Rh particles, both Pt and Rh functioned as active components and each made a significant contribution to CH_4 /CO/NO conversions. Conversely, the incorporation of additives (La^{3+} , Zr^{4+} , and Ba^{2+}) into Cat3 meant that the La^{3+} ions could enhance the dispersion of active components and active sites, thus improving the catalytic activity [19]. The additives might also work to disperse the precious metals to form a discontinuous phase, reducing the interactions between the noble metals and the support, thus improving the reducibility of the catalyst, as seen in the H_2 -TPR results. Moreover, the insertion of Zr^{4+} ions into the ceria–zirconia lattice created a higher concentration of lattice defects and thus improved the O_2 -mobility [24,26]. The presence of monoclinic ZrO_2 in Cat3 is also important; it has been reported that monoclinic ZrO_2 shows higher activity for CH_4 oxidation [37,38]. In addition, Cat3 had the highest Ce^{3+}/Ce ratio, which also assisted in the conversion of NO [36]. In this work, Cat3 exhibited remarkable catalytic performance, and therefore has potential applications in stoichiometric NGV exhaust purification.

4. Conclusions

Pt–Rh bimetallic catalysts prepared by a co-impregnation method exhibited significantly inferior catalytic activity compared with those materials fabricated by physically mixing Pt and Rh catalyst powders. This was possibly because of the influence of strong Pt–Rh interactions on the oxidation state and

reducibility of the noble metals brought about by co-impregnation. The co-impregnation technique also appears to have generated large Pt-enriched bimetallic Pt–Rh particles that blocked active Rh sites and thus decreased catalytic activity. The catalysts made by physically mixing Pt and Rh presented a homogeneous mixture of Pt and Rh sites on their surfaces, such that both Pt and Rh made significant contributions to CH_4 /CO/NO conversions, thus enhancing the three-way activity. Added Zr^{4+} was incorporated into the CeO_2 – ZrO_2 lattice, increasing the concentration of structural defects, improving the O_2 -mobility and raising the surface Ce^{3+}/Ce ratio. This produced more oxygen vacancies and a greater degree of charge imbalance on the catalyst surfaces, which would be beneficial to the redox transformation between Ce^{3+} and Ce^{4+} , thus enhancing NO conversion.

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Graphical Abstract

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Catalytic performance of Pt–Rh/CeZrYLa+LaAl with stoichiometric natural gas vehicles emissions

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Pt–Rh catalysts supported on CeZrYLa+LaAl were prepared by three different methods and assessed for application in stoichiometric natural gas vehicle exhaust purification. The additive-promoted, physically mixed Pt–Rh catalysts exhibited excellent catalytic activity and a wide air-to-fuel working-window.

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Pt-Rh/CeZrYLa+LaAl催化剂用于理论空燃比天然气汽车尾气净化

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摘要: 采用共沉淀法制备了CeZrYLa+LaAl纳米复合载体, 以三种方法制备了一系列Pt-Rh/CeZrYLa+LaAl催化剂. 对所制样品进行了N₂吸附-脱附、粉末X射线衍射、X射线光电子能谱和H₂程序升温还原的表征. 并考察了三种方法所制得催化剂的理论空燃比天然气汽车尾气净化性能. 结果表明, 三个催化剂的活性顺序为Cat3 ≈ Cat2 > Cat1, 其中Cat3具有最低的CO和NO起燃温度(T_{50}), 分别为114 °C和149 °C, 最低的CH₄和CO完全转化温度(T_{90}), 分别为398 °C和179 °C, 以及最佳的CH₄和CO温度特性, ΔT ($T_{90}-T_{50}$)值分别为34 °C和65 °C. Cat2具有最低的CH₄起燃温度(342 °C)和最低的NO完全转化温度(174 °C). Cat1具有最差的转化活性, 说明物理混合法制备的催化剂(Cat3和Cat2)性能优于共浸渍法制备的催化剂(Cat1). 这是由于物理混合法制备的催化剂, Pt和Rh均匀分散在载体表面, 两者物理接触共同参与CH₄/CO/NO三种污染物的转化. 相反, 共浸渍法制备的催化剂, Pt和Rh之间存在较强的相互作用, 改变了Pt的电子状态, 而且形成了表面Pt富集的Pt-Rh双金属颗粒覆盖了Rh活性位, 从而降低催化活性; 同时, 对于通过物理混合法并进一步添加助剂所制备的Cat3, XRD结果显示助剂Zr⁴⁺进入了钨钨固溶体晶格, 产生晶格缺陷; XPS结果显示Cat3具有最高的Ce³⁺/Ce比例. 这些都有利于提高催化剂的氧流动性, 从而提高催化剂活性并拓宽空燃比窗口.

关键词: 铂-铑; 纳米复合CeZrYLa+LaAl; 钨-钨-钨助剂; 理论空燃比天然气汽车; 尾气净化

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