Modification of $Ce_{0.67}Zr_{0.33}O_2$ mixed oxides by coprecipitated/impregnated Co: Effect on the surface and catalytic behavior of Pd only three-way catalyst

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ABSTRACT

The promotional effect of cobalt oxide on the catalytic performance and the physicochemical properties of Pd only three-way catalysts and $Ce_{0.67}Zr_{0.33}O_2$ mixed oxides (CZ) prepared by co-precipitation and impregnation methods have been investigated. It is worthwhile to note that the role of Co significantly depends on the method of Co doping in the CZ. The introduction of cobalt oxide by co-precipitation exhibits significant influence on the catalytic activity of Pd only three-way catalyst with enhancing textural and structural properties, compared to the introduction of cobalt oxide by impregnation method. Furthermore, CZ doped with cobalt oxide by co-precipitation results in the formation of more homogeneous ternary solid solution, which promotes the metal–support interaction between CZ and cobalt metal and improves oxygen storage capacity (OSC) of samples. It also proves that the textural and structural properties of supports can affect the reducibility and oxygen storage capacity of samples at low temperature.

1. Introduction

Three-way catalysts (TWCs) have been widely used to reduce pollutant emissions from gasoline engine powered vehicles [1]. In recent years, typical TWCs formulations have included Pd as the active metal, fluorite-type oxides, for example ceria–zirconia (CeO_2–ZrO_2), as promoters and alumina as support as well as other minor components mainly present in order to enhance thermal stability [1,2]. CeO_2–ZrO_2 mixed oxides have been considered as an outstanding oxygen storage materials in TWCs, which aim at simultaneously and efficiently to reduce NO and to oxidize CO and hydrocarbons (HC) in a narrow window in automotive exhaust [3–5]. As more and more rigorous emission regulations are being applied, ceria–zirconia materials with better oxygen storage capacity (OSC) and redox properties are required for the further development of durable, highly active and versatile TWCs [6,7]. Modification of ceria–zirconia materials by the introduction of a third, cheaper metal would appear to offer a viable solution from both an economical and catalytical point of view [8,9]. In recent studies, the introduction of transition metals into TWCs [10–12], which promoted the oxygen storage capac-

ity and the redox property at lower temperature and achieved the lower light-off temperature during the cold start phase, has earned much attention in Pd only TWCs area [13–15]. The effects of doping transition metals on the structure and redox properties have also been widely investigated. It was reported that the substitution of zirconium atoms by iron ones generates oxygen vacancies into the tetragonal network [16]. Terribile [17] reported that both MnO_x and CuO at low loading dissolve within the ceria–zirconia lattice, which strongly influences the redox behavior of the catalysts by promoting low-temperature reduction of Ce^{4+}. A further promotional effect on catalytic property is observed with the introduction of MnO_x and CuO dissolved into CeO_2–ZrO_2 lattice. Moreover, homogeneity of the solid solution, structural features and composition are key factors in successful redox catalyst design. Furthermore, ternary solid solution could improve the thermal stability and enhance the migration and exchange of oxygen species by storing and releasing oxygen.

In this work, cobalt oxide was introduced to modify CZ not only by co-precipitation but also by impregnation method. In particular, we investigated the effects of introducing Co into CZ lattice by two methods, focusing on the structural properties, oxygen storage capacity, redox properties and catalytic activity. X-ray diffraction (XRD), N_2 adsorption, H_2-temperature programmed reduction (H_2-TPR) and oxygen storage capacity (OSC) have been performed to pursue this aim. The catalytic performance of Pd-only three-way catalyst was also investigated.

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2. Experimental

2.1. Catalyst preparation

$Ce_{0.67}Zr_{0.33}O_2$ mixed oxides doped with cobalt oxide was prepared by a co-precipitation route. The doping of cobalt oxide was fixed at 5 wt.%. $ZrO(NO_3)_2$, $Ce(NO_3)_3$ and $Co(NO_3)_2 \cdot 6H_2O$ were used as metal precursors. The required amounts of $ZrO(NO_3)_2$, $Ce(NO_3)_3$ and/or $Co(NO_3)_2 \cdot 6H_2O$ were dissolved in water. The ammonia water or NaOH solution was added dropwise to the solution of metal precursors to maintain the pH at about 9.5. The obtained slurry was aged at room temperature for 12 h, and then filtered, washed with deionized water and dried under supercritical condition in ethanol (265 °C, 7.0 MPa) for 2 h. The samples were calcined at 500 °C in air for 4 h to obtain support. All of the obtained supports were pressed into pellets, crushed and sieved to 40–60 meshes. The supports were designated as CZ, CZCo, respectively.

Co/CZ support containing 5% of cobalt oxide in weight was prepared by the impregnation of the powder CZ in aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$ overnight. The resulting sample was dried at 110 °C for 4 h and calcined at 500 °C in air for 4 h. The obtained support was pressed into pellets, crushed and sieved to 40–60 meshes.

Three supported Pd only three-way catalysts with Pd content of 0.5 wt.% were also prepared by incipient wetness impregnation method, in which H_2PdCl_4 solution was used as Pd precursor. The resulting precipitate was reduced using hydrazine hydrate solution for 2 h, washed several times with deionized water until no Cl^- ions detected in the filtered solution, and then dried at 110 °C for 4 h followed by calcination at 500 °C for 2 h to obtain catalyst. The catalysts were designated as Pd/CZ, Pd/CZCo and Pd/Co/CZ, respectively.

2.2. Catalytic activity measurement

Catalytic tests were carried out with a fixed-bed continuous flow reactor. The catalyst (0.2 ml) was held in a quartz tube by packing quartz wool at both ends of the catalyst bed. The reaction mixture containing NO (0.1%)–NO_2 (0.03%)–C_3H_6 (0.067%)–C_3H_8 (0.033%)–CO (0.75%)–O_2 (0.745%) and balance Ar was fed to the reactor at a GHSV of 43,000 h^{-1}. The effluent gas was analyzed by on-line Fourier transform infrared spectrophotometer (BRUKER EQ55) equipped with a multiple reflection transmission cell (Infrared Analysis Inc.; path length 10.0 m). All spectra were taken at a resolution of 2 cm^{-1} for 128 scans. The air/fuel ratio experiments were carried out at 400 °C. The concentration of O_2 was adjusted in the tests of air/fuel ratio from 850 to 8440 ppm. The λ value of the simulated exhaust, which represents the ratio between the available oxygen and the oxygen needed for full conversion to CO_2, H_2O and N_2, is defined as λ $\{2[O_2] + [NO] + 2[NO_2]\}/\{9[HC] + [CO]\}$, $\lambda = 1$ was at stoichiometry and the corresponding concentration of O_2 was 7450 ppm.

2.3. Characterization techniques

X-ray diffraction (XRD) measurement was performed on an ARL X'TRA X-ray Diffractometer (Thermo Eelctron Corporation, USA), with Cu Kα radiation, operating at 40 kV and 40 mA. Spectra were collected using a step size of 0.04° and a counting time of 5 s per angular abscissa in the range of 20–80° (2θ).

The textural properties were determined by N_2 adsorption using TriStar Π 3020 (Micromeritics Inc.). The sample (0.15 g) was degassed at 200 °C for 3 h under vacuum, and N_2 adsorption was carried out at −196 °C.

The redox behavior of supports and catalysts was examined by hydrogen temperature-programmed reduction (H_2-TPR). Each sample (50 mg) was pretreated at 300 °C for 30 min in air and cooled

down to room temperature or −40 °C in N_2. The gas flow was then switched to 5% H_2/Ar, and the temperature was raised to 900 °C at a rate of 10 °C min^{-1}. The consumption of H_2 was monitored using a thermal conductivity detector (TCD).

Oxygen storage capacity measurement was carried out using CHEMBET-3000 (Quantachrome Co.). The sample (100 mg) was reduced at 550 °C for 60 min in H_2 (10 ml/min), then cooled down to 200 °C and flushed with He (30 ml/min) for 20 min. A given amount of O_2 (0.15 ml) was pulsed every 5 min until the intensity of the peak was a constant value.

3. Results and discussion

3.1. Catalytic performance of catalysts

CZ doped with cobalt oxide was prepared by a co-precipitation and impregnation methods, respectively. In order to compare the differences between the two doping methods, the Pd only three-way catalysts were examined by FTIR to analyze the gas phase after reaction. The CO, HC, NO and NO_2 conversions as a function of temperature under stoichiometric $CO + HC + NO_x + O_2$ reaction conditions over these catalysts are shown in Fig. 1. The results demonstrate the promoting role of doping cobalt oxide, compared to that reported previously by us for the monometallic Pd catalysts [18]. These data reveal an important promoting effect of Co on this system that appears to be almost dependent on the method of cobalt oxide doping in the support. The introduction of cobalt oxide by co-precipitation and supercritical dried exerts significant influence on the catalytic activity of Pd only three-way catalyst, corresponding to the enhancement of CO, HC, NO and NO_2 conversions, respectively. However, different effects are induced by the presence of cobalt oxide through impregnation method. The presence of Co produces an apparent increase in CO oxidation and NO_2 reduction over the Pd/Co/CZ catalyst, but has a detrimental effect on the HC oxidation and NO reduction. Table 1 presents the light-off temperature ($T_{50\%}$) and full-conversion temperature ($T_{90\%}$) of CO, HC, NO and NO_2 and the width of the window (W) over three catalysts. In our experiments, we also test the conversions of CO, HC and NO_x under different air/fuel ratios (λ = 0.2, 0.4, 0.6, 0.8, 1.0, 1.04, 1.07, 1.1, 1.15). The left side of the theoretical stoichiometric value (λ = 1) is lean oxygen, and the right is rich oxygen. W (λ value width) acts as another scale to evaluate catalyst property when CO, HC and NO_x conversions all reach to 80% under rich and lean conditions. For example, the upper limit of the stoichiometric windows is limited by NO_x conversion under rich condition; the lower limit is limited by CO conversion under lean conditions for all samples. The upper limit subtracting the lower limit of λ is W value. Furthermore, the wider the W value is, the broader the three-way working window is. As can be seen from Table 1 that the presence of Co decreases the light-off temperature and promotes the catalytic activity of Pd/CZCo catalyst. Moreover, the increasing value of W indicates that the window of activity becomes wider. In contrast, the presence of Co in Pd/Co/CZ catalyst only decreases the light-off temperature of CO and NO_2. Furthermore, the window of activity hardly changes by comparison with that of Pd/CZ catalyst. From the above discussions, we have concluded that the introduction of cobalt oxide by co-precipitation and supercritical dried method exhibits better influence on the catalytic activity of Pd only three-way catalyst, compared to that of introduced by impregnation method.

3.2. XRD and N_2 adsorption

To have some insight into the difference catalytic activity between the two doping methods, textural and structural properties were investigated by XRD and N_2 adsorption and the results
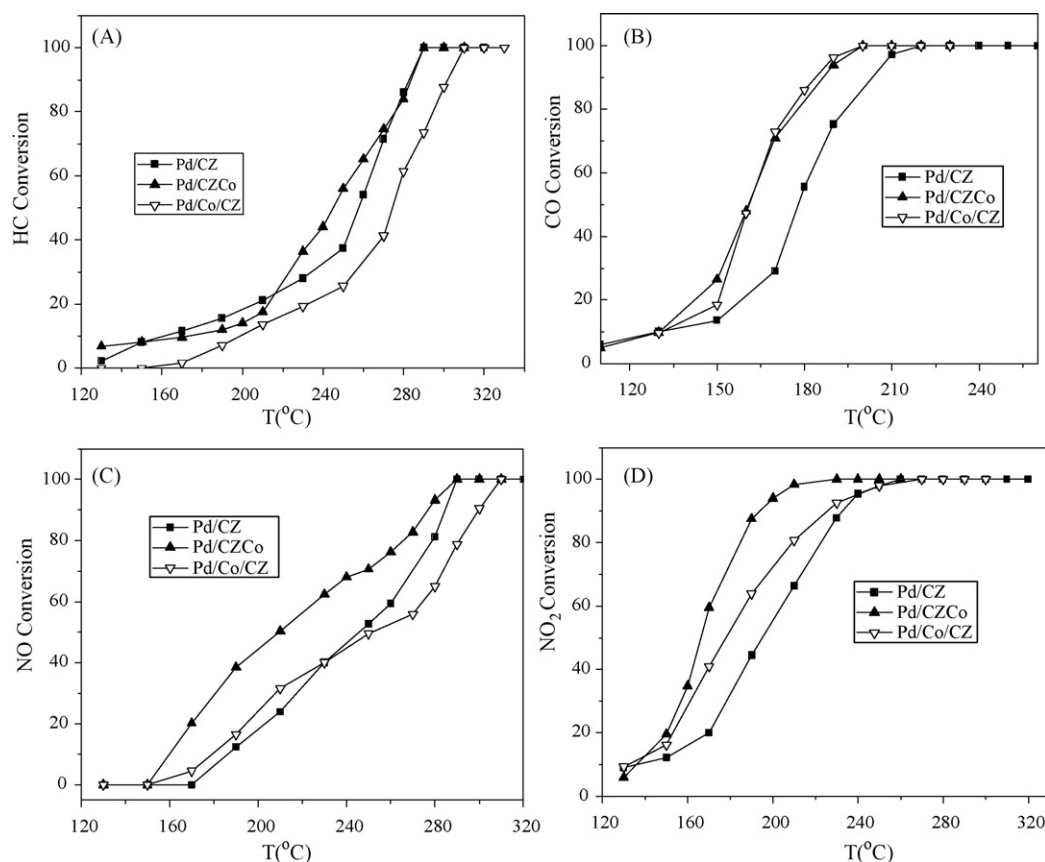
Fig. 1. Conversion of HC (A), CO (B), NO (C) and NO_2 (D) as a function of reaction temperature under stoichiometric $CO + NO_x + HC + O_2$. Reaction condition: NO (0.1%)–NO_2 (0.03%)–C_3H_6 (0.067%)–C_3H_8 (0.033%)–CO (0.75%)–O_2 (0.745%) in Ar over catalysts.

Table 1
Light-off and full-conversion temperature of CO, HC, NO and NO_2 and the width of the window (W) over catalysts.

Catalyst	$T_{50\%}$ (°C)				$T_{90\%}$ (°C)				W
	HC	CO	NO	NO_2	HC	CO	NO	NO_2	
Pd/CZ	258	178	246	195	283	204	284	233	0.221
Pd/CZCo	245	161	210	167	283	186	276	193	0.253
$\geq T^a$	13	17	36	28	0	18	8	40	
Pd/Co/CZ	275	161	250	178	302	183	299	225	0.223
$\geq T$	−17	17	−4	17	−19	21	15	8	

[a] $\geq T = T(Pd/CZ) - T(Pd/CZCo\ or\ Pd/Co/CZ)$.

are shown in Figs. 2 and 3 and Table 2. Fig. 2 displays the XRD patterns of the CZ doped by cobalt oxide with different methods. All of the diffractograms in Fig. 2 show the main reflections typical of a cubic fluorite-structured material, with fcc unit cells at 28.7°, 33.2°, 47.9°, and 56.7°, corresponding to the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes [19,20]. No peak splitting that would indicate the presence of two phases could be detected for CZCo support, and therefore, the diffraction patterns demonstrate the formation of a single solid solution like ceria–zirconia phase. Table 2 presents the textural and structural properties of the samples. The cell parameter of CZCo is 0.5356 nm, which is smaller than CZ (0.5407 nm). It may be due to the fact that the incorporation Co^{2+}/Co^{3+} into

CZ lattice by replacing of Ce^{4+}/Ce^{3+} or Zr^{4+} leads to the shrinkage of the lattice parameter. It is worth pointing out that the introduction of Co by co-precipitation and supercritical dried enters into the ceria–zirconia lattice and forms the homogeneous ternary solid solution. However, for Co/CZ support, XRD reveals evidence of phase segregation for the mixed oxide, with the presence of clearly characteristic Co_3O_4 phase peaks. Moreover, the diffraction peaks become sharper and more symmetrical, indicating the growth of the nanocrystals [21], and the crystallite size increases from 7.9 to 8.8 nm in Table 2. The cell parameter of CoCZ is 0.5412 nm, which is bigger than CZ (0.5407 nm). Compared to that of CZCo, the increase of crystallite size and cell parameter indicates that a segregation

Table 2
Textural and structural properties of $Ce_{0.67}Zr_{0.33}O_2$ mixed oxides doped cobalt oxide by different methods.

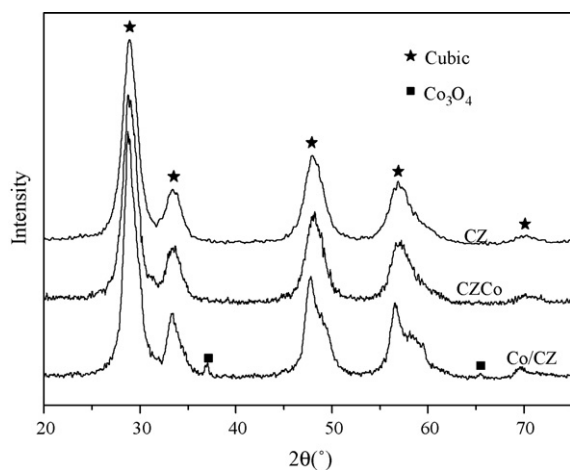| Sample	Average pore diameter (nm)	Pore volume (m³/g)	S_{BET} (m²/g)	Crystallite size (nm)	Lattice parameter (nm)
CZ	20.70	0.7281	122.0	7.9	0.5407
CZCo	23.86	0.9443	110.5	7.4	0.5356
Co/CZ	16.90	0.5230	100.4	8.8	0.5412

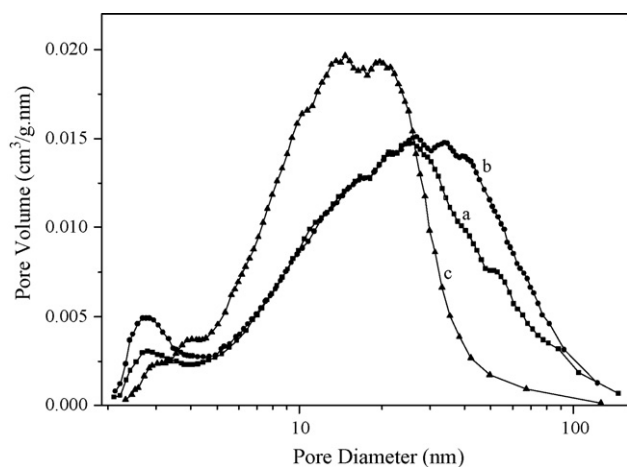**Fig. 2.** XRD characterization of $Ce_{0.67}Zr_{0.33}O_2$ mixed oxides doped by cobalt oxide.

Fig. 3. Pore-size distribution of $Ce_{0.67}Zr_{0.33}O_2$ mixed oxides doped by cobalt oxide. (a) CZ, (b) CZCo, (c) Co/CZ.

Fig. 4. H_2 consumption profiles during H_2-TPR over supports.
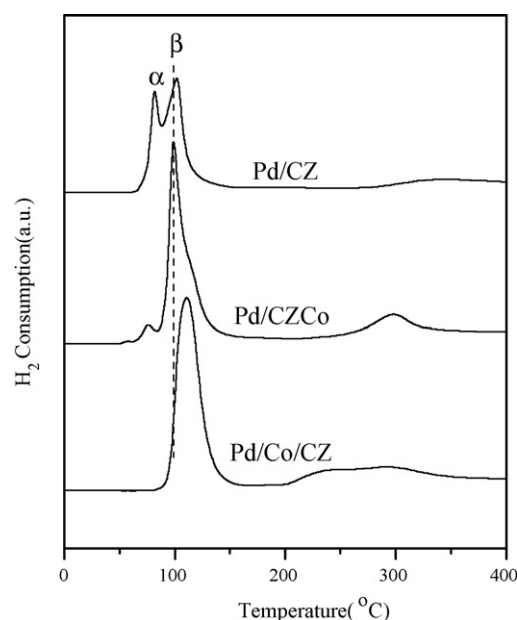
Fig. 5. H_2 consumption profiles during H_2-TPR over catalysts.

of the cobalt oxide eventually dissolves in the lattice with the formation of weak signal due to crystalline Co_3O_4, which makes the formation of non-homogeneous solid solution. It proves that the introduction of Co by co-precipitation and supercritical dried forms more homogeneous ternary solid solution than that prepared by impregnation method, corresponding to the decrease of the crystallite size. From Table 2, we also conclude that the introduction of Co by two methods does not increase the surface area of samples. However, the average pore diameter increases for CZCo in favor of the adsorption/desorption of reaction species. It may be one of the reasons of activity enhancement. The pore-size distribution of CZ doped by cobalt oxide is also presented in Fig. 3. It is obvious to point out that the introduction of Co by co-precipitation and supercritical dried increases the average pore diameter. Based on above experimental facts, we speculate that ceria–zirconia doped with cobalt oxide by co-precipitation and supercritical dried results in more active Pd only three-way catalysts with enhanced textural and structural properties.

3.3. H_2-TPR

We investigated the reduction properties of the samples by H_2-TPR; the H_2 consumption profiles obtained over supports are plotted in Fig. 4. H_2 consumption must be attributed to the reduction of Ce^{4+} to Ce^{3+}, because Zr^{4+} is a nonreducible cation. For CZ, two strong reduction peaks appear in its TPR profile with a

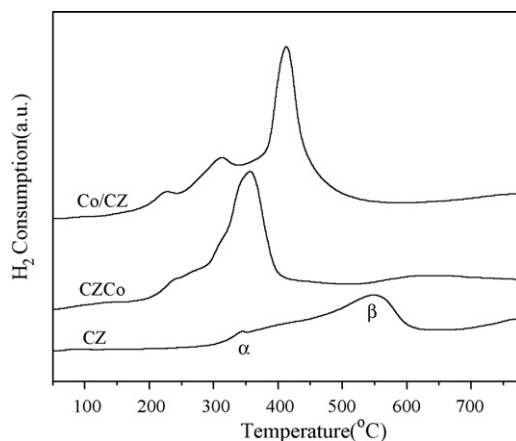maximum at 345 and 560 °C (referred to α, β), which ascribed to the reduction of surface and subsurface oxygen [20,22,23]. What is more, there is no clear distinction between the surface and subsurface peaks, because oxygen located within the subsurface comes to the surface as surface oxygen is consumed. This type of profile is characteristic of materials with good oxygen mobility [20]. Moreover, the reduction peaks of cobalt oxide are not clearly observed because of the reduction of the more easily reducible support. Obviously, the two peaks are shifted to lower temperature by the presence of Co, considering the effect of strong metal–support interaction between CZ and cobalt metal. Moreover, compared to Co/CZ, CZCo presents rather lower reduction temperature, indicating that CZ doped with Co by co-precipitation and supercritical dried exhibits better reduction properties than that of prepared by impregnation method. Combined with the structure of the supports, we also estimate that CZ doped with cobalt oxide by co-precipitation and supercritical dried results in the formation of more homogeneous ternary solid solution, which promotes the metal–support interaction between CZ and cobalt oxide.

Fig. 5 presents H_2 consumption profiles during H_2-TPR over the Pd only three-way catalysts. Pd/CZ catalyst shows two peaks α and β at ca. 81 and 101 °C, which has been associated to the

Table 3
Oxygen storage capacity of samples calculated as μmol O_2/g of sample at 200 °C.

Samples	OSC (μmol O_2/g)
CZ	358.8
CZCo	558
Co/CZ	504.6
Pd/CZ	431.7
Pd/CZCo	765.6
Pd/Co/CZ	683

reduction of PdO species highly dispersed on the surface of the support and formed on the interaction between PdO and the support [24,25], respectively. For Pd/CZCo catalyst, the intensity of β peak is higher than that of Pd/CZ, indicating that the introduction of Co by co-precipitation and supercritical dried clearly promotes the interaction between PdO and the support. Although the reduction peak also presents on the Pd/Co/CZ catalyst, it shifts to higher temperature. Moreover, there is small reduction peak α over Pd/CZCo, which is associated to the reduction of PdO species highly dispersed on the surface of the support. Furthermore, the area of the H_2 consumption peaks (α and/or β) of PdO species over catalysts is larger than that of theoretical area. It should be taken into account that the reduction of the most easily reducible support is caused by the spillover of H_2 onto the support. The presence of noble metals strongly modifies these features due to hydrogen activation by the metal and consequent migration to the support (spillover) favoring reduction of the support at lower temperature. Although the reduction peak also presents on the Pd/Co/CZ catalyst, it shifts to higher temperature. It indicates that the interaction between noble metal and support over Pd/CZCo is stronger than that over Pd/Co/CZ, due to the formation of ternary solid solution in CZCo support. To summarise, the characterization of supports and catalysts suggests that both these materials have a cubic fluorite structure, and that CZ incorporates Co cations into its framework. This incorporation of foreign cations enhances the reduction properties of samples. A case point is that the reduction modification of reduction/oxidation can result in a more homogeneous structure and improve OSC performance [23]. Therefore, we have concluded that CZ doped with cobalt oxide by co-precipitation and supercritical dried leads to the formation of more homogeneous ternary solid solution, with better reduction properties compared to that preparing by impregnation method.

3.4. OSC

The oxygen storage capacity (OSC) of sample is regarded as one of the most important parameters to evaluate the applicability of materials to rapidly switching between lean and rich conditions [26–29]. Furthermore, the light-off catalytic performance is improved by the enhancement of oxygen mobility of the sample at low temperature. Table 3 displays the oxygen storage capacity of samples calculated as μmol O_2/g of sample at 200 °C. The introduction of Co clearly promotes the oxygen storage capacity of supports, especially doped by co-precipitation and supercritical dried method. The present study clearly shows the relationship between the OSC and local structure around Ce, Zr and Co in mixed oxides. The OSC increases by enhancing the homogeneity of the atoms in the Ce–Zr–Co–O ternary solid solution. The enhancement of the homogeneity of the ternary solid solution could ease the valence change of the Ce ($Ce^{4+} \rightarrow Ce^{3+}$) [30]. We have postulated that the enhancement of the homogeneity of the ternary solid solution and the modification of the oxygen environment would be the source for the OSC improvement.

Compared to that of supports, oxygen storage capacity of catalysts clearly increases. We have known that defects play another role in the oxygen storage process when noble metal is supported on ceria–zirconia, which is the usual application in practice

[23]. Oxidation of noble metal in Pd/ceria–zirconia catalyst reflects electron transfer from metal to ceria–zirconia, indicating slightly reduced Ce associated with oxygen vacancy formation [23,31]. Due to the higher potential of the Ce^{4+}/Ce^{3+} couple (1.61 eV) compared with the Pd^{2+}/Pd^0 couple, oxygen vacancies play important roles of carriers to determine the oxygen spillover and back-spillover processes at noble metal/ceria–zirconia interfaces [32]. It explains the improvement of oxygen storage capacity of catalysts compared to that of supports. Moreover, CZ doped with cobalt oxide by co-precipitation and supercritical dried results in the enhancement of oxygen storage capacity of samples, compared to that of preparing by impregnation method.

4. Conclusion

CZ doped with cobalt oxide was prepared by a co-precipitation and impregnation methods, respectively. In order to compare the differences between the two doping methods, the effect of cobalt oxides on the catalytic performance and the physicochemical properties of Pd only three-way catalysts and CZ has been studied by using catalytic test, X-ray diffraction, N_2 adsorption, H_2-temperature programmed reduction and oxygen storage capacity. We have concluded that the role of Co significantly depends on the method of Co doping in the CZ. The introduction of cobalt oxide by co-precipitation and supercritical dried appears to exert significant influence on the catalytic activity of the catalyst, corresponding to the enhancement conversions of CO, HC, NO and NO_2. Moreover, the presence of Co decreases the light-off temperature and promotes the catalytic activity of Pd/CZCo catalyst. The value of W increases that indicates the window of activity becomes wider. In contrast, the presence of Co in Pd/Co/CZ catalyst only decreases the light-off temperature of CO and NO_2. Furthermore, the window of activity hardly changes by comparison with Pd/CZ catalyst. It is of interesting to note that CZ doped with cobalt oxide by co-precipitation and supercritical dried results in more active only Pd three-way catalyst with enhanced textural and structural properties, compared to the introduction of cobalt by impregnation method. From the XRD and N_2 adsorption results, we have obtained that the introduction of Co by co-precipitation and supercritical dried enters into the CZ lattice and forms the homogeneous ternary solid solution and increases the average pore diameter. However, for Co/CZ support, XRD reveals the evidence of phase segregation of the mixed oxide, with the presence of clearly characteristic Co_3O_4 phase peaks. We also investigated the redox properties of samples by H_2-TPR. Combination with the structure of the supports, we have concluded that CZ doped with cobalt oxide by co-precipitation and supercritical dried leads to the formation of more homogeneous ternary solid solution, with better redox properties compared to that of preparing by impregnation method. Moreover, the enhancement of the homogeneity of the ternary solid solution could ease the valence change of the Ce ($Ce^{4+} \rightarrow Ce^{3+}$). Therefore, CZ doped with cobalt oxide by co-precipitation and supercritical dried results in the formation of more homogeneous ternary solid solution, with enhancement oxygen storage capacity of support and catalyst, compared to that of preparing by impregnation method. It also proves that the textural and structural properties of support can affect the reducibility and oxygen storage capacity of samples at low temperature.

References

[1] E.S.J. Lox, B.H. Engler, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Environmental Catalysis, Wiley–VCH, 1999, p. 1.
[2] R.M. Heck, R. Farrauto, Catalytic Air Pollution Control, Wiley–Interscience, New York, 2002 (Chaps. 6 and 12).
[3] N. Hickey, P. Fornasiero, J. Kašpar, J.M. Gatica, S. Bernal, J. Catal. 200 (2001) 181–193.
[4] H.S. Gandhi, G.W. Graham, R.W. McCabe, J. Catal. 216 (2003) 433–442.
[5] R. Di Monte, J. Kašpar, Catal. Today 100 (2005) 27–35.
[6] B.M. Reddy, P. Bharali, G. Thrimurthulu, P. Saikia, L. Katta, S.E. Park, Catal. Lett. 123 (2008) 327–333.
[7] G.P. Osorio, S.F. Moyado, V. Petranovskii, A. Simakov, Catal. Lett. 110 (2006) 53–60.
[8] B. Coq, F. Figueras, J. Mol. Catal. A 173 (2001) 117–134.
[9] D.H. Kim, S.I. Woo, J.M. Leeb, O.B. Yang, Catal. Lett. 70 (2000) 35–41.
[10] M. Fernández-García, A. Martínez-Arias, A. Iglesias-Juez, A.B. Hungría, J.A. Anderson, J.C. Conesa, J. Soria, J. Catal. 214 (2003) 220–233.
[11] X. Courtois, V. Perrichon, Appl. Catal. B 57 (2005) 63–72.
[12] L. Jia, M. Shen, J. Wang, X. Chu, J. Wang, Z. Hu, J. Rare Earths 26 (2008) 523–527.
[13] A.B. Hungría, N.D. Browning, R.P. Erni, M. Fernández-García, J.C. Conesa, J.A. Pérez-Omil, A. Martínez-Arias, J. Catal. 235 (2005) 251–261.
[14] A.B. Hungría, M. Fernández-García, J.A. Anderson, A. Martínez-Arias, J. Catal. 235 (2005) 262–271.
[15] A. Martínez-Arias, M. Fernández-García, A.B. Hungría, A. Iglesias-Juez, J.A. Anderson, Catal. Today 126 (2007) 90–95.
[16] V.R. Mastelaro, V. Briois, D.P.F. de Souza, C.L. Silva, J. Eur. Ceram. Soc. 23 (2003) 273–282.
[17] D. Terribile, A. Trovarelli, C. de Leitenburg, A. Primavera, G. Dolcetti, Catal. Today 47 (1999) 133–140.
[18] B. Zhao, Q. Wang, C. Ge, G. Li, R. Zhou, Chin. J. Catal. 30 (2009) 407–413.
[19] D. Terribile, A. Trovarelli, J. Llorca, C. de Leitenburg, G. Dolcetti, Catal. Today 43 (1998) 79–88.
[20] I. Atribak, A. Bueno-López, A. García-García, J. Catal. 259 (2008) 123–132.
[21] C. Li, X. Gu, Y. Wang, Y. Wang, Y. Wang, X. Liu, G. Lu, J. Rare Earths 27 (2) (2009) 211–215.
[22] G.L. Markaryan, L.N. Ikryannikova, G.P. Muravieva, A.O. Turakulova, B.G. Kostyuk, E.V. Lunina, V.V. Lunin, E. Zhilinskaya, A. Aboukais, Colloids Surf. A 151 (1999) 435–447.
[23] M. Zhao, M. Shen, J. Wang, J. Catal. 248 (2007) 258–267.
[24] P.S. Lambrou, A.M. Efstathiou, J. Catal. 240 (2006) 182–193.
[25] S. Zuo, R. Zhou, Micropor. Mesopor. Mater. 113 (2008) 472–480.
[26] J. Kašpar, P. Fornasiero, N. Hickey, Catal. Today 77 (2003) 419–449.
[27] J. Kašpar, P. Fornasiero, J. Solid State Chem. 171 (2003) 19–29.
[28] P. Fornasiero, R. Di Monte, G.R. Rao, J. Kašpar, S. Meriani, A. Trovarelli, M. Graziani, J. Catal. 151 (1995) 168–177.
[29] F. Dong, A. Suda, T. Tanabe, Y. Nagai, H. Sobukawa, H. Shinjoh, M. Sugiura, C. Descorme, D. Duprez, Catal. Today 93–95 (2004) 827–832.
[30] Y. Nagai, T. Yamamoto, T. Tanaka, S. Yoshida, T. Nonaka, T. Okamoto, A. Suda, M. Sugiur, Catal. Today 74 (2002) 225–234.
[31] X. Wu, J. Fan, R. Rui, D. Weng, Chem. Eng. J. 109 (2005) 133–139.
[32] C. Bozo, N. Guilhaume, J.-M. Herrmann, J. Catal. 203 (2001) 393–406.