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# *Comparative Study on Nano-Sized 1 wt% Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and 1 wt% Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> Catalysts for a Single Stage Water Gas Shift Reaction*

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# Comparative Study on Nano-Sized 1 wt% Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and 1 wt% Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> Catalysts for a Single Stage Water Gas Shift Reaction

Dae-Woon Jeong · Hari S. Potdar · Hyun-Seog Roh

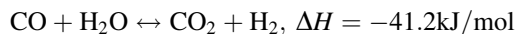
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**Abstract** A comparative study on nano-sized Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalysts in a single stage water gas shift (WGS) reaction was carried out. These catalysts were prepared by impregnating 1 wt% Pt on nano-sized cubic (Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>) and tetragonal (Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub>) supports. Both catalysts have been applied to WGS under identical conditions to understand beneficial effect of cubic/tetragonal phases of Ce<sub>(1-x)</sub>Zr<sub>(x)</sub>O<sub>2</sub>. 1 wt% Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> exhibited higher CO conversion than 1 wt% Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub>. In addition, 1 wt% Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalyst showed relatively stable activity with time on stream. The high activity/stability of 1 wt% Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalyst was correlated to its higher Pt dispersion and easier reducibility.

**Keywords** Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> · Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> · Single stage water gas shift (WGS) · Cubic/tetragonal phase

## 1 Introduction

Hydrogen (H<sub>2</sub>) is a clean energy carrier emitting only water [1, 2]. If H<sub>2</sub> is produced from hydrocarbons, CO should be removed from the synthesis gas mixture. Recently, the interest in the water gas shift (WGS) reaction has grown significantly as a result of recent developments in fuel cell technology [3]. WGS is a crucial step to remove CO and to produce additional H<sub>2</sub> from synthesis gas:



In general, WGS process consists of Fe<sub>2</sub>O<sub>3</sub>/Cr<sub>2</sub>O<sub>3</sub> based high temperature shift (HTS) and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> based low temperature shift (LTS). This process can successfully reduce CO levels to less than 1% in a large scale H<sub>2</sub> plant [4]. However, the conventional WGS unit is not suitable for a compact reformer due to restrictions in volume, weight and cost [5]. Thus, it is necessary to develop advanced catalysts for single stage WGS, which can do HTS and LTS at the same time.

Many attempts, therefore, have been made to develop active catalysts based on noble/transition metals supported on reducible oxides which can overcome those limitations [6–10]. Among these catalysts, Pt supported on ceria, and mixed oxides of ceria–zirconia have been identified as promising catalysts for WGS [10–14]. It is reported that both metal and support play an important role in WGS [4]. WGS is believed to occur either through an associative or a redox type mechanism [4]. In the associative mechanism, CO reacts with the bridging surface OH on the oxide to generate formate (HCOO) intermediate species [15]. By further reaction with another surface OH, the formate species is transformed into carbonate while H<sub>2</sub> is liberated. The simultaneous decomposition of carbonate and H<sub>2</sub>O will generate CO<sub>2</sub> and restore the bridging surface OH groups. The role of the metal is to facilitate formation of OH groups on the oxide surface during the reduction process and to help to decompose intermediate formate species. In the redox type mechanism, CO is adsorbed on the metal and is oxidized at the metal/oxide interface with the formation of CO<sub>2</sub> [12]. The oxide surface is then reoxidized by H<sub>2</sub>O. Thus, the nature of metal and support play crucial roles in controlling the activity/stability of the catalyst during WGS. Characteristics of Ce<sub>(1-x)</sub>Zr<sub>(x)</sub>O<sub>2</sub> supports not only affect adsorption properties of the Pt particles but also help to improve Pt dispersion. In addition,

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the metal to support interaction is also significant for WGS [16]. Recently, it is reported that Pt/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> (consisting of both cubic and tetragonal phases) gave higher activity/stability than Pt/CeO<sub>2</sub> in WGS [9, 16].

The cubic phase of Ce<sub>(1-x)</sub>Zr<sub>(x)</sub>O<sub>2</sub> has higher oxygen storage capacity (OSC), reducibility and enhancement in capability of redox couple (Ce<sup>4+</sup> ↔ Ce<sup>3+</sup>) than the tetragonal phase of Ce<sub>(1-x)</sub>Zr<sub>(x)</sub>O<sub>2</sub> [17–19]. Therefore, it is necessary to study activity/stability of 1 wt% Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> (cubic phase) and Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> (tetragonal phase) in WGS. It will be useful to study the effect of the nano-sized cubic/tetragonal Ce<sub>(1-x)</sub>Zr<sub>(x)</sub>O<sub>2</sub> supports on controlling the reducibility and oxygen mobility [20]. Moreover, Ce<sub>(1-x)</sub>Zr<sub>(x)</sub>O<sub>2</sub> supports will help to reduce the formation of surface carbonate species, which deactivate the WGS catalyst [21].

The objective of the present study is to evaluate activity/stability of Pt/Ce<sub>(1-x)</sub>Zr<sub>(x)</sub>O<sub>2</sub> catalysts by employing ceria–zirconia supports having either cubic structure (CeO<sub>2</sub> rich composition) or tetragonal structure (ZrO<sub>2</sub> rich composition) in WGS.

## 2 Experimental

### 2.1 Catalyst Preparation

Nano-sized Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> supports were prepared by one step co-precipitation/digestion method [22]. Stoichiometric quantities of zirconyl nitrate (20 wt% ZrO<sub>2</sub> basis, MEL Chemicals) and cerium nitrate (99%, Aldrich) were dissolved in distilled water to get a solution containing Ce and Zr cations. To this solution 15 wt% KOH solution was added drop-wise at 80 °C to attain a pH of 10.5. The precipitates were aged at 80 °C for 3 days. After that, they were washed with distilled water several times and then air-dried for 2 days followed by drying at 110 °C for 6 h. The prepared supports were pre-calcined at 500 °C for 6 h. 1 wt% Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalysts were prepared by an incipient wetness impregnation method with Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (99%, Aldrich). The prepared catalysts were calcined at 500 °C for 6 h.

### 2.2 Characterization

The BET surface area was measured by nitrogen adsorption at −196 °C using an ASAP 2010 (Micromeritics). The average particle size was calculated from the BET data by using the equation:  $d = 6/\rho A$ , where  $\rho$  is the theoretical density of the material and  $A$  is the surface area of the powder. The XRD patterns were recorded using a Rigaku D/MAX-IIIIC diffractometer (Ni filtered Cu–K radiation, 40 kV, 50 mA). The crystallize size was estimated using

the Debye–Scherrer equation. CO-chemisorption was conducted in a BEL-METAL-3 (BEL Japan Inc.). The calcined catalyst was reduced at 400 °C for 1 h in 20% H<sub>2</sub>/Ar flow. From the chemisorbed amount, the Pt dispersion was calculated by assuming the adsorption stoichiometry of one CO per Pt surface atom (CO/Pt<sub>s</sub> = 1) [23]. Temperature programmed reduction (TPR) experiments were carried out in a BEL-CAT (BEL Japan Inc.). Typically, 0.1 g of sample was loaded into a quartz reactor. The TPR was performed using 10% H<sub>2</sub> in Ar with a heating rate of 10 °C min<sup>−1</sup>, from 20 to 600 °C. The sensitivity of the detector was calibrated by reducing known weight of NiO.

### 2.3 Catalytic Reaction

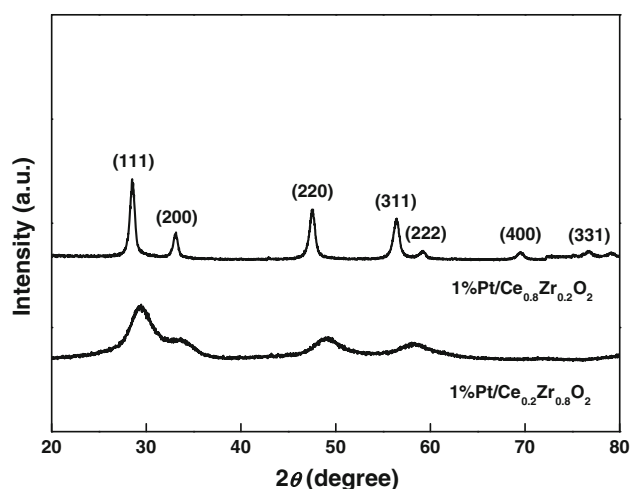
Activity tests were carried out from 200 to 360 °C under atmospheric pressure in a fixed-bed micro-tubular quartz reactor with an inner diameter of 4 mm. The catalyst charge was 47 mg. T-union was employed at the exit of quartz reactor to install a thermocouple. A thermocouple was inserted into the catalyst bed to measure the reaction temperature. Prior to each catalytic measurement, the catalyst was reduced in 5% H<sub>2</sub>/N<sub>2</sub> from room temperature to 400 °C at a heating rate of 3.3 °C min<sup>−1</sup> and then the temperature was maintained for 1 h. Afterwards, the temperature was decreased to 200 °C. The simulated reformed gas consisted of 6.4 vol% CO, 7.1 vol% CO<sub>2</sub>, 0.7 vol% CH<sub>4</sub>, 43.0 vol% H<sub>2</sub>, 28.4 vol% H<sub>2</sub>O, and 14.4 vol% N<sub>2</sub>. The feed H<sub>2</sub>O/(CH<sub>4</sub> + CO + CO<sub>2</sub>) ratio was intentionally fixed at 2.0 because a H<sub>2</sub>O/CH<sub>4</sub> ratio is typically 3 in steam reforming of methane (SRM: H<sub>2</sub>O + CH<sub>4</sub> = 3H<sub>2</sub> + CO) to avoid coke formation [24–31].

A gas hourly space velocity (GHSV) of 45,515 h<sup>−1</sup> was used to screen the catalysts in this study. Water was fed using a syringe pump and was vaporized at 150 °C upstream of the reactor. The product gas was chilled, passed through a trap to condense the residual water, and then analyzed on-line using an Agilent micro-gas chromatograph.

## 3 Results and Discussion

### 3.1 Characterization

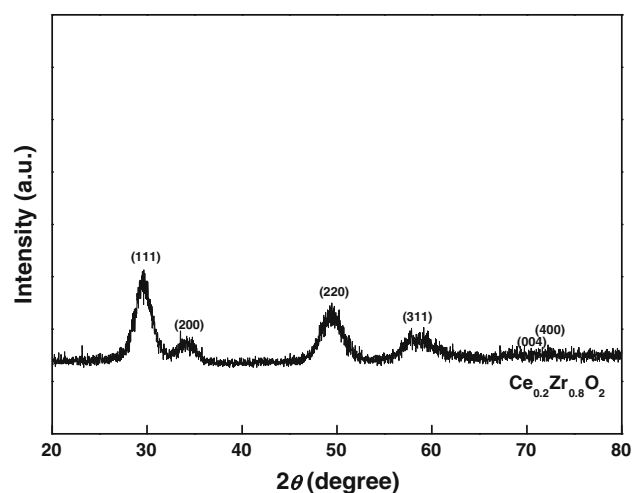
Figure 1 depicts XRD patterns of Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalysts, respectively. The reflections corresponding to Pt metal particles can not be detected due to low loading content of Pt ≤ 1 wt%. All the observed reflections of Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalyst are indexed to face centered cubic (fcc) fluorite structure (Fm3m space group) [22, ICDD Card No. 28-0271]. The broad symmetric peaks indicate nano-crystalline nature of Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> support.



**Fig. 1** XRD patterns of Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalysts

The calculated lattice parameter,  $a_0$  for Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalyst is 5.35 Å which agrees with the reported lattice parameter of the cubic phase of Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> [22]. On the contrary, Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalyst indicates tetragonal phase, although there is no splitting between [004] and [400] planes at  $2\theta = 75^\circ$ . In addition, each peak reflection is shifted towards higher angles due to the insertion of Zr ions with the larger size (0.97 Å) into the lattice of CeO<sub>2</sub>. This observation is consistent with the report that 25 mol% ZrO<sub>2</sub> or more is sufficient to obtain a fully tetragonal phase in solid solution of nano-sized ceria–zirconia [32, ICDD Card No. 80-0785]. Recently, Fuentes et al. [32] reported that nano-crystalline ceria–zirconia solid solution exhibited either cubic or tetragonal phase depending upon CeO<sub>2</sub> content. They applied Rietveld refinement method to know the phases present in the nano crystalline ceria–zirconia solid solution. It is established by them that the tetragonal phase is present in nano-crystalline ceria–zirconia solid solution if ZrO<sub>2</sub> content is  $\geq 25$  mol%. To confirm this issue, we heated the sample at higher temperature i.e. 800 °C for 6 h in air and XRD pattern was taken. Figure 2 shows improved crystallinity, indicating thereby homogeneity within the catalyst. Moreover, 400 reflections observed in the XRD pattern of Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> is symmetric but the same is broad and asymmetric in that of Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub>. It means that 400 reflections are split into 004 and 400 as is normally observed in the tetragonal phase of zirconia rich solid solution of ceria–zirconia. This observation suggests that the catalyst supported on Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> has a tetragonal structure. It is well known that the addition of ZrO<sub>2</sub> into the lattice of CeO<sub>2</sub> lowers the crystallinity of ceria–zirconia solid solution.

Table 1 summarizes catalyst surface area, support surface area, and support crystallite size. Generally, the BET surface areas of catalysts are relatively lower than those of



**Fig. 2** XRD pattern of Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> support calcined at 800 °C for 6 h

**Table 1** Characteristics of Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalysts

Catalyst	Catalyst S.A. (m <sup>2</sup> g <sup>-1</sup> )	Support S.A. (m <sup>2</sup> g <sup>-1</sup> )	Support crystallite size (nm)
Pt/Ce <sub>0.8</sub> Zr <sub>0.2</sub> O <sub>2</sub>	119	137	10.4 <sup>a</sup> , 6.3 <sup>b</sup>
Pt/Ce <sub>0.2</sub> Zr <sub>0.8</sub> O <sub>2</sub>	244	244	2.3 <sup>a</sup> , 3.9 <sup>b</sup>

<sup>a</sup> Measured by XRD

<sup>b</sup> Calculated from BET

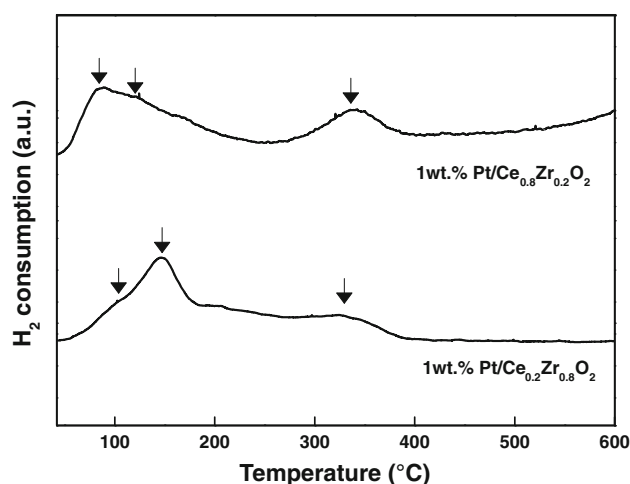
**Table 2** CO chemisorption results of Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalysts

Catalyst	Pt dispersion (%)	Pt S.A. (m <sup>2</sup> g <sup>-1</sup> )	Pt crystallite size (nm)
Pt/Ce <sub>0.8</sub> Zr <sub>0.2</sub> O <sub>2</sub>	66.9	1.65	1.69
Pt/Ce <sub>0.2</sub> Zr <sub>0.8</sub> O <sub>2</sub>	55.7	1.38	2.03

supports, indicating that the BET surface area decreases after Pt loading. The BET surface area of Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> is twice higher than that of Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> but the crystallite size of the tetragonal Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> support is about four times smaller than that of the cubic Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> support. This could be related to the tendency of the crystals to form agglomerates to lower their surface energy. It is evident from the Table 1 that the support with the higher BET surface area does not yield smaller crystallite sizes.

Table 2 summarizes CO chemisorption results of Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalysts. It is interesting to note that Pt dispersion of Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> (66.9%) is higher than that of Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> (55.7%) even though the BET surface area of the former is half the value of the latter. This indicates that Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> with cubic support





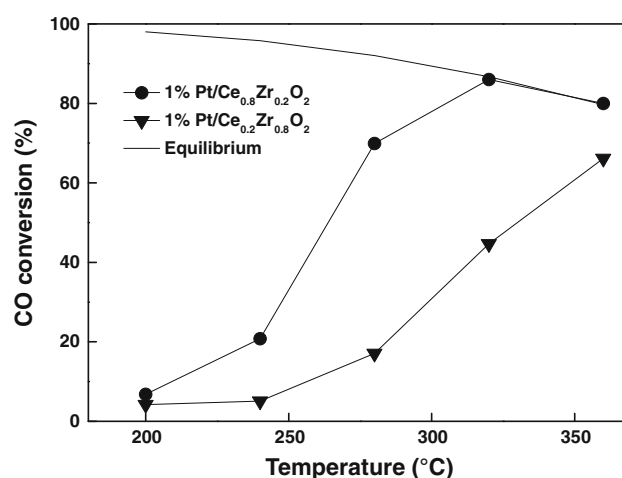
**Fig. 3** TPR patterns of Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalysts

helps to achieve a higher Pt dispersion. As a consequence, Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> shows higher Pt surface area and smaller Pt crystallite size than Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub>. It is interesting to note that the value of CO consumption on the Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> i.e. 29.3 (error < 0.05)  $\mu\text{mol}_{\text{CO}}/\text{g}_{\text{cat}}$  is higher than that of 24.1 (error < 0.05)  $\mu\text{mol}_{\text{CO}}/\text{g}_{\text{cat}}$  on the Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalyst under the similar treatment conditions, even though the bridging OH groups are formed during the reduction step on the ceria–zirconia catalysts.

Figure 3 shows TPR patterns of Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalysts. Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalyst has three reduction peaks at 85, 120 and 340 °C, respectively. The first peak, appearing at 85 °C is attributed to the reduction of surface PtO<sub>x</sub> species. The first peak overlaps the second peak. The second peak is assigned to the reduction of PtO<sub>x</sub> species with an interaction with the support. The last peak at 340 °C is assigned to the reduction of bulk CeO<sub>2</sub> from the cubic Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> support [33, 34]. On the other hand, Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalyst shows the first peak at 100 °C with low intensity. This peak is due to the reduction of surface PtO<sub>x</sub> species. The second prominent peak, appearing at 150 °C, is attributable to PtO<sub>x</sub> species interacting with the support. The last peak at 330 °C is assigned to the reduction of bulk CeO<sub>2</sub> from tetragonal Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> support. According to TPR results, the reduction of surface PtO<sub>x</sub> species of Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> is easier than that of Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub>.

### 3.2 Reaction Results

Figure 4 depicts CO conversion profile as a function of reaction temperature over Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalysts. Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalyst exhibited higher CO conversion than Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalyst within the temperature range between 240 and 360 °C. This is possibly due to the presence of more irreducible ZrO<sub>2</sub> in



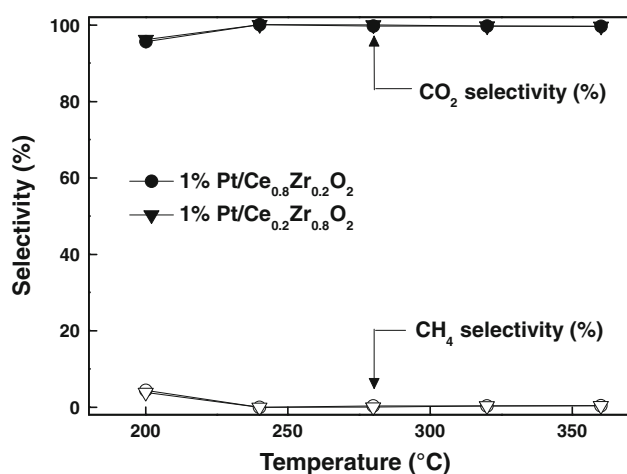
**Fig. 4** CO conversion with reaction temperature over Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalysts (H<sub>2</sub>O/(CH<sub>4</sub> + CO + CO<sub>2</sub>) = 2.0; GHSV = 45,515 h<sup>-1</sup>)

**Table 3** TOFs and reaction rate results of Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalysts

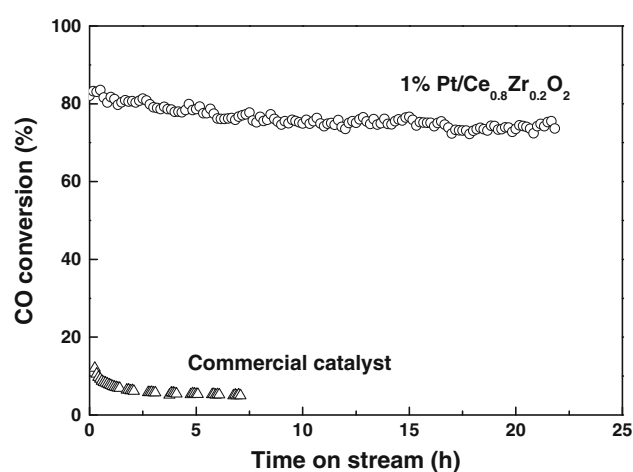
Catalyst	Temperature (°C)	Turnover frequency (s <sup>-1</sup> )	Reaction rate ( $\mu\text{mol}_{\text{CO}}/\text{g}_{\text{cat}}$ s)
Pt/Ce <sub>0.8</sub> Zr <sub>0.2</sub> O <sub>2</sub>	200	0.073	2.52
	240	0.223	7.65
Pt/Ce <sub>0.2</sub> Zr <sub>0.8</sub> O <sub>2</sub>	240	0.066	1.89
	280	0.222	6.34

Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalyst and low OSC of the tetragonal Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> phase [18, 19]. At the reaction temperature of 320 °C, Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalyst reached almost equilibrium CO conversion even at the GHSV of 45,515 h<sup>-1</sup>, which is 15 times higher than the typical WGS reaction condition. At this temperature, CO conversion of Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalyst is about twice higher than that of Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalyst. The activation energies ( $E_a$ ) over Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalysts are 56 and 71 kJ mol<sup>-1</sup>, respectively. To compare the reactivity of these two catalysts, turnover frequencies (TOFs) and reaction rate are given in Table 3. TOF and reaction rate of the catalyst with cubic phase at 240 °C are much higher than those of the catalyst supported on tetragonal phase. The outstanding activity of Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalyst is correlated to its higher Pt dispersion, easier reducibility, lower activation energy, and higher OSC of the cubic Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> support [18, 19].

Figure 5 shows selectivity to CO<sub>2</sub> and CH<sub>4</sub> with reaction temperature over Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalysts. At the reaction temperature of 200 °C, the methanation reaction occurred very slightly. Above 240 °C, however, 100% selectivity to CO<sub>2</sub> was maintained for both



**Fig. 5** Selectivity to CO<sub>2</sub> and CH<sub>4</sub> with reaction temperature over Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalysts (H<sub>2</sub>O/(CH<sub>4</sub> + CO + CO<sub>2</sub>) = 2.0; GHSV = 45,515 h<sup>-1</sup>)



**Fig. 6** CO conversion with time on stream over Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and commercial catalyst (H<sub>2</sub>O/(CH<sub>4</sub> + CO + CO<sub>2</sub>) = 2.0; T = 320 °C; GHSV = 45,515 h<sup>-1</sup>)

**Table 4** Comparative data on CO conversion over Pt/Ce<sub>(1-x)</sub>Zr<sub>(x)</sub>O<sub>2</sub> catalysts for WGS

Catalyst	GHSV (h <sup>-1</sup> )	CO conversion (Reaction temp.)	Reference
1 wt% Pt/Ce <sub>0.80</sub> Zr <sub>0.20</sub> O <sub>2</sub>	45,515	78% (300 °C)	Present work
1 wt% Pt/Ce <sub>0.75</sub> Zr <sub>0.25</sub> O <sub>2</sub>	45,000	63% (300 °C)	[4]
1 wt% Pt/Ce <sub>0.50</sub> Zr <sub>0.50</sub> O <sub>2</sub>	45,000	68% (300 °C)	[4]
1 wt% Pt/Ce <sub>0.60</sub> Zr <sub>0.40</sub> O <sub>2</sub>	45,000	68% (300 °C)	[4]
1 wt% Pt/Ce <sub>0.25</sub> Zr <sub>0.75</sub> O <sub>2</sub>	45,000	37% (300 °C)	[4]
4 wt% Pt/Ce <sub>0.56</sub> Zr <sub>0.44</sub> O <sub>2</sub>	40,000	70% (300 °C)	[15]
4 wt% Pt/Ce <sub>0.44</sub> Zr <sub>0.56</sub> O <sub>2</sub>	40,000	79% (300 °C)	[35]

catalysts. This indicates that both catalysts can selectively convert CO into CO<sub>2</sub> without the methanation reaction.

Table 4 compares reaction data on CO conversion over Pt/Ce<sub>(1-x)</sub>Zr<sub>(x)</sub>O<sub>2</sub> catalysts with that over Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalyst tested in this study [4, 16, 35]. It should be noted that 1 wt% Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalyst showed the highest CO conversion among 1 wt% Pt/Ce<sub>(1-x)</sub>Zr<sub>(x)</sub>O<sub>2</sub> catalysts.

To check stability of Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalyst with time on stream, CO conversion data was collected for 20 h. As a reference, a commercial catalyst (Fe/Cr) was also tested under the same reaction conditions. Figure 6 shows CO conversion with time on stream over Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and commercial catalysts. For the Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalyst, the CO conversion was decreased to 75% after 20 h. This is possibly due to the catalyst deactivation by (i) sintering of Pt particles (ii) embedding of Pt by reduced support oxide and (iii) formation of carbonate species blocking the active site at the interface region. In the case of the commercial catalyst, it showed very low CO conversion at the GHSV of 45,515 h<sup>-1</sup>. This is due to the fact that conventionally the

WGS reaction has been carried out at the GHSV of 3,000 h<sup>-1</sup>. In another word, the commercial catalyst is not suitable for the single stage WGS, which requires high intrinsic activity at very high GHSV.

## 4 Conclusions

Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalyst exhibits higher CO conversion than Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalyst due to higher Pt dispersion, easier reducibility, lower activation energy, and higher OSC of the cubic Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> support. Above the reaction temperature of 240 °C, Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalyst shows 100% CO<sub>2</sub> selectivity in WGS. Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalyst can be a promising candidate catalyst for the single stage WGS, which requires high intrinsic activity at very high GHSV.

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