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# Aqueous phase reforming of glycerol using highly active and stable Pt<sub>0.05</sub>Ce<sub>x</sub>Zr<sub>0.95-x</sub>O<sub>2</sub> ternary solid solution catalysts

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Graphical abstract



#### Highlights

- Pt<sub>0.05</sub>Ce<sub>x</sub>Zr<sub>0.95-x</sub>O<sub>2</sub> ternary solid solutions were synthesized by a simple one-step method by our group for the first time.
- $Pt_{0.05}Ce_xZr_{0.95-x}O_2$  ternary solid solutions are highly selective and stable for APR reaction.
- Pt<sub>0.05</sub>Ce<sub>0.475</sub>Zr<sub>0.475</sub>O<sub>2</sub> was found to be very active and stable in APR of glycerol, had the highest carbon to gas conversion, H<sub>2</sub> yield, H<sub>2</sub> selectivity and stability.
- This is the first application of the stable  $Pt_{0.05}Ce_xZr_{0.95-x}O_2$  ternary solid solutions not only for the APR of glycerol but for any other catalytic reaction.

**Abstract:** The aqueous phase reforming (APR) of glycerol is an attractive yet challenging pathway to convert abundant biomass into value added hydrogen. Pt catalysts have received attention due to their ability to produce hydrogen-rich gas under APR conditions. In this work, the conversion of glycerol into hydrogen is demonstrated using  $Pt_{0.05}Ce_xZr_{0.95-x}O_2$  (x=0, 0.29, 0.475, 0.66 and 0.95) solid solution catalysts. Both characteristic (XRD, BET, H<sub>2</sub>-TPR, CO-chemisorption, TEM and XPS) and reactivity measurements were used to investigate the activity of the catalysts. Results indicated that reactivity depended on the Ce/Zr ratio, which in turn affected the Pt oxidation state, active metal dispersion and surface area, and particle size. Among these catalysts  $Pt_{0.05}Ce_{0.475}Zr_{0.475}O_2$  showed the highest carbon to gas conversion (95%), highest H<sub>2</sub> yield (93%), highest H<sub>2</sub> selectivity (98%) and at least 50 h of stability. The overall catalytic performance decreased in the order  $Pt_{0.05}Ce_{0.475}Zr_{0.475}O_2 > Pt_{0.05}Ce_{0.29}Zr_{0.66}O_2 > Pt_{0.05}Ce_{0.29}O_2 > Pt_{0.05}Ce_{0.29}O_2 > Pt_{0.05}Ce_{0.29}O_2.$ 

**Keywords:**  $PtCeZrO_2 \cdot Solid$  solution catalysts  $\cdot$  Glycerol  $\cdot$  Aqueous phase reforming  $\cdot$  Renewable hydrogen

#### Introduction

The environmental crises such as global warming and climate change caused by the fossil fuel utilization, as well as the depletion of petroleum resources call for alternative energy sources. Consequently, sustainable clean fuels generated from renewable sources, such as biomass, have come to attention. In this sense, hydrogen is considered as one of the most promising forms of future clean energy. The demand for hydrogen is also growing due to technological progress in the fuel cell industry [1].

Aqueous-phase reforming (APR), developed by Dumesic and co-workers in 2002, is one of the technically feasible approaches that has been proposed as an attractive new route for generating hydrogen-rich fuel gas in a single step from various oxygenated hydrocarbons including glycerol, ethylene glycol, sorbitol, glucose, methanol, and ethanol under relatively mild reaction temperatures of 200–250°C and pressures in the range of 20–50 bar [2-8]. The current industrial process for hydrogen production is the high-temperature steam reforming of hydrocarbons. APR has many advantages compared with conventional steam reforming that include a higher energy efficiency and elimination of undesirable reaction products that are formed at high temperatures. Additionally, the low reaction temperatures used in APR favor the water-gas-shift reaction (WGS) resulting in a hydrogen-rich gas with low CO content (<300 ppm) making it suitable for direct use in proton exchange membrane (PEM) fuel cell systems [9].

According to the APR mechanism reported by Dumesic and co-workers [2-8], the desired catalyst in APR should have highly activity for both the cleavage of the C-C bonds and for the WGS reaction while at the same time be able to inhibit competing parallel and series reactions including C-O bond cleavage and the methanation/Fischer-Tropsch reactions that would significantly reduce the hydrogen yield. Of the metal catalysts employed in the APR process, the group VIII metals, particularly platinum, have shown high activity for hydrogen production because of their high activity towards C-C bond cleavage and WGS reactions and low selectivity towards the methanation reaction [2-4,10,11]. The metal oxide carriers could significantly influence both the overall activity and the product selectivity in APR reactions [4,11,12]. Catalyst stability in APR is a challenging issue [13]. When conventional metal oxides such as Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, SiO<sub>2</sub>, ZnO and TiO<sub>2</sub> are used as support materials, their porous structures could either deteriorate by sintering or their specific surface areas could decrease due to phase transfer under APR conditions thus restricting their use as support materials [6,11,14]. Much is understood for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Under the hydrothermal conditions,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is known to be hydrated and crystallized resulting in crystalline boehmite and this process can affect the catalytic activity or the products formed [12]. Therefore, the support material should have a high hydrothermal stability to be used in the APR reaction.

The use of ceria and zirconia based mixed oxide supports has been reported recently for a variety of reactions including WGS [15-17] and preferential CO oxidation [18,19] with the mixed oxides demonstrating a better performance compared with the individual oxides due to their higher hydrothermal stability as well as oxygen storage capacity. In the case of APR reaction,  $Pt/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts modified with ceria and ceria-zirconia show significantly higher H<sub>2</sub> yield and selectivity [20,21].

The APR of model compounds using a variety of nano-catalysts supported on metal oxide supports has been reported by many investigators [6,11,12,22,23]. Decreasing the average diameter of the Pt particles in the Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts increased the production of H<sub>2</sub> and CO<sub>2</sub> while CO production was decreased [24] indicating that the rate of the water gas shift reaction increased with decreasing metal particle size. These results provide valuable insight for development of new nano-catalysts. Catalyst activity is highly influenced by the catalyst preparation method [9,25]. Dry or wet impregnation methods that are most frequently used for preparation of APR catalysts could commonly result in the agglomeration of the active phase on the support especially when a high loading of metal precursors are used leading to the formation of large size particles.

Classifying multi-metallic catalysts into different structures including hetero-structures, core-shell structures, solid solutions, ensembles and segregations, most investigated catalysts for the APR reaction are hetero-structures. Different examples for bi-metallic catalysts are shown in Figure 1 [26]. In the core-shell structure, different types of metal ions are reduced by their tendency for nucleation. First, the

ions of the core are reduced. Metal atoms of the shell prefer to nucleate and grow surrounding the core, since separate nucleation is difficult for them. Individual nucleation and growth of different kinds of metal atoms can occur to form hetero-structures and segregations under certain circumstances. When metal-metal bonds form, homogeneous mixture of different metals is made. According to the distribution of distinct metal atoms either ensembles or solid solutions are produced. Catalysts in present study are of solid solution type.

Figure 1. Different types of bi-metallic catalysts [26]

In the present study, the APR reaction has been investigated using a series of novel, highly active and stable  $Pt_{0.05}Ce_xZr_{0.95-x}O_2$  ter-metallic (ternary) solid solutions synthesized by controlled coprecipitation technique, with emphasis on the influence of  $Zr^{4+}$  dopant on the properties and performance of the catalysts. To this end, the catalysts were extensively characterized by using XRD, BET, H<sub>2</sub>-TPR, CO-chemisorption, TEM, and XPS analyses. The catalytic activity, selectivity, and stability over time of the catalysts were determined for the APR of glycerol. This is the first application of  $Pt_{0.05}Ce_xZr_{0.95-x}O_2$  ternary solid solution catalysts not only for the APR of glycerol but for any other catalytic reaction.

#### **Experimental Section**

**Catalyst preparation.** All reagent chemicals were of analytical grade and used without further purification. Distilled water was used to prepare all aqueous solutions. The novel nano-sized solid solution catalysts which were studied here are  $Pt_{0.05}Ce_xZr_{0.95}.xO_2$  (x=0, 0.29, 0.475, 0.66 and 0.95) where x represented the nominal weight fraction of Ce in catalyst. Samples were prepared by controlled precipitation or co-precipitation methods. Hexachloroplatinic acid, (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O), cerium nitrate [Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O] and zirconium oxychloride (ZrOCl<sub>2</sub>·8H<sub>2</sub>O) were used as precursor salts, and sodium hydroxide (NaOH) was used as precipitant. The co-precipitation process was conducted by the dropwise addition of 1 M solution of sodium hydroxide under constant stirring into an aqueous solution of appropriate amount of precursor salts. The temperature was kept at 60°C and to ensure complete precipitation the addition of NaOH was continued until the pH reached a value of 12. To achieve the desired structure of nano-catalysts, in addition to temperature and pH, the rate of addition of precipitating agent was set so that the entire process of precipitation lasted 16 h. The mixture was further aged at 25°C for 12 h. Samples were then filtered and washed using hot distilled water until no Cl<sup>-</sup> was detected by AgNO<sub>3</sub> solution. The precipitate was then dried at 100°C for 24 h and calcined at

 $600^{\circ}$ C for 5 h. For the purpose of comparison, pure CeO<sub>2</sub> and ZrO<sub>2</sub> samples were also prepared following the same procedure.

Catalyst characterization. X-ray diffraction (XRD) patterns were obtained using a PW3040/60 X'Pert PRO MPD (PANalytical) diffractometer equipped with a Cu K $\alpha$  radiation source ( $\lambda$ = 1.5406 Å) and operating at 40 kV and 40 mA. A continuous mode was used for collecting data in the 20 range of 20° to 100° at a scanning speed of 10° min<sup>-1</sup>. Brunauer-Emmett-Teller (BET) surface areas of the catalysts were evaluated from nitrogen adsorption-desorption isotherms at -196°C using a Belsorp mini II apparatus. Samples were gassed out at 120°C for 15 h prior to analysis. Transmission electron microscopy (TEM) micrographs were obtained using a Zeiss EM900 transmission electron microscope with accelerating voltage of 80 keV. TEM images were analyzed using the Digital Micrograph software package (Gatan, Inc.) with at least 100 particles imaged and analyzed for each sample to determine the average diameter. H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) was performed on Micromeritics TPR/TPD 2900 apparatus. The samples were first purged with helium at 300°C for 90 min. After cooling to room temperature, the flowing gas was switched to a 5 vol% H<sub>2</sub>/Ar and the catalyst was heated from 25°C to 800°C with a ramp of 10°C min<sup>-1</sup>. The amount of H<sub>2</sub> consumption during the process of reduction was measured by a thermal conductivity detector (TCD). Chemisorption uptakes were measured using pulse methods (BELCAT-A, BEL, Japan). Prior to the chemisorption analysis, samples were treated in  $O_2$  flow by increasing the temperature to 300°C at 30°C min<sup>-1</sup> and holding at 300°C for 15 min. The sample was then reduced in H<sub>2</sub> flow at 500°C for 1 h and subsequently cooled to 25°C at 30°C min<sup>-1</sup> in order to remove the chemisorbed hydrogen. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Physical Electronics Systems Quantum 2000 spectrometer using monochromatic Al Ka radiation.

**Catalyst performance.** APR of glycerol was carried out in a continuous tubular fixed bed reactor (Figure 2). Glycerol was chosen as a model compound since it has a C:O ratio of 1:1 commonly found in biomass-derived sugar compounds. 250 mg of the powder catalyst was packed into the reactor that was a vertical stainless steel tube with an inner diameter of 5 mm. In order to hold the catalyst bed in position, two plugs of quartz wool were used. The reactor was placed inside a tube furnace equipped with type K thermocouple and a PID temperature controller. The reactor pressure was controlled using a dual phase, diaphragm-type back pressure regulator (Equilibar, LLC). Prior to the start of each experiment, the catalyst was reduced in-situ under H<sub>2</sub> of 50 mL min<sup>-1</sup> for 2 h at 500 °C using a temperature ramp rate of 1 °C min<sup>-1</sup>. The reactor was subsequently purged with 100 mL min<sup>-1</sup> flow of N<sub>2</sub> for 5 h. After cooling to the reaction temperature of 250°C, the reactor pressure system was set to the desired pressure of 50 bar. A Waters 510 HPLC digital pump was used to feed the glycerol solution (WHSV of 2.45 h<sup>-1</sup>) into the reactor. Once the reactor system had stabilized (about 2 h after the start of

a run), the reaction products were analyzed. The gaseous products were swept by  $N_2$  as a carrier gas and analyzed continuously using an on-line Varian CP-3800 gas chromatograph that was equipped with a Hayesep Q and a Molecular Sieve column. For each experiment, at least five gas samples were analyzed and checked for relative standard deviations. Only four peaks representing H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>, were detected in the product gases. The liquid effluent collected in a gas-liquid separator was subsequently analyzed for elemental carbon by a Shimadzu HPLC instrument equipped with a Rezex RCM-Monosaccharide column using ultrapure deionized water as an eluent at 0.5 mL min<sup>-1</sup>. The catalyst performance was evaluated based on H<sub>2</sub> yield, H<sub>2</sub> selectivity, CH<sub>4</sub> selectivity, carbon conversion to gas, and glycerol conversion which calculated according to:

 $H_{2} \text{ yield} = \frac{\text{molar flow rate of } H_{2} \text{ produced experimentally}}{7 \times \text{glycerol molar flow rate fed into the reactor}} \times 100$   $CO_{2} \text{ yield} = \frac{\text{molar flow rate of } CO_{2} \text{ produced experimentally}}{3 \times \text{glycerol molar flow rate fed into the reactor}} \times 100$   $CH_{4} \text{ selectivity} = \frac{CH_{4} \text{ produced experimentally}}{\text{total number of C atoms in gas product}} \times 100$   $H_{2} \text{ selectivity} = \frac{2 \times H_{2} \text{ produced experimentally}}{\text{total number of H atoms in gas product}} \times 100$   $Carbon \text{ to gas conversion} = \frac{\text{number of C atoms in gas product}}{\text{number of C atoms fed into the reactor}} \times 100$   $Glycerol \text{ conversion} = \frac{\text{amount of glycerol removed from liquid phase}}{\text{amount of glycerol in feedstock}} \times 100$ 

All data are mean values of  $\geq$ 3 experiments and error bars indicate one standard deviation.

Figure 2. Schematic of the reactor system

#### **Results and Discussion**

**XRD.** The XRD patterns for CeO<sub>2</sub>, ZrO<sub>2</sub> and Pt<sub>0.05</sub>Ce<sub>x</sub>Zr<sub>0.95-x</sub>O<sub>2</sub> (x=0, 0.29, 0.475, 0.66 and 0.95) samples are shown in Figure 3(A). A closer look in the 27-32° [Figure 3(B)] and 32-37° [Figure 3(C)] regions allows one to observe that the pattern of Pt<sub>0.05</sub>Ce<sub>0.95</sub>O<sub>2</sub> and Pt<sub>0.05</sub>Zr<sub>0.95</sub>O<sub>2</sub> did not correspond to any of the pure metal oxide standards and showed a slight shift of characteristic pure oxide peaks towards higher angles. This suggests that some  $Zr^{4+}$  (0.84 Å) and Ce<sup>4+</sup> (0.97 Å) ions had been displaced by smaller Pt<sup>2+</sup> (0.80 Å) or Pt<sup>4+</sup> (0.63 Å) ions, leading to a contraction of CeO<sub>2</sub> and ZrO<sub>2</sub> lattices. Thus,

it should cause a decrease of the value of the lattice parameter (Table 1). Also, the pattern of the  $Pt_{0.05}Ce_xZr_{0.95-x}O_2$  (x=0.29, 0.475 and 0.66) nano-structures did not correspond to any of the  $Pt_{0.05}Ce_{0.95}O_2$  and  $Pt_{0.05}Zr_{0.95}O_2$  catalysts. The XRD patterns of  $Pt_{0.05}Ce_xZr_{0.95-x}O_2$  (x=0.29, 0.475 and 0.66) catalysts are similar to that of  $Pt_{0.05}Ce_{0.95}O_2$  but are shifted to higher angles with increasing Zr content. This indicates that  $Ce^{4+}$  (0.97 Å) is partially substituted with  $Zr^{4+}$  (0.84 Å) in  $Pt_{0.05}Ce_xZr_{0.95-x}O_2$  (x=0.29, 0.475 and 0.66) catalysts to form a ternary solid solution.

Table 1 summarizes the size of the crystallites and their lattice parameters as evaluated by Scherrer's equation (The shape factor was assumed to be 0.9. For cubic phase, lattice parameter is calculated using plane with Miller indices (3 1 1) and for tetragonal phase,  $\alpha = \beta$  and  $\gamma$  parameters are calculated using planes with Miller indices (2 0 0) and (1 0 1), repectively.) Particle sizes in the nanometer range were obtained for each material. Characteristic tetragonal and cubic phases were detected in pure ZrO<sub>2</sub> and CeO<sub>2</sub>, respectively. As shown in Table 1, nano-crystalline Pt<sub>0.05</sub>Ce<sub>x</sub>Zr<sub>0.95-x</sub>O<sub>2</sub> solid solutions had either cubic (ICDD card No. 80-0785) or tetragonal (ICDD card No. 28-0271) phase depending upon ceria content. Furthermore, the average grain size from Scherrer's formula was used as reference. The average crystallite size for the tetragonal phase gradually decreased from 9.2 nm (Pt<sub>0.05</sub>Zr<sub>0.95</sub>O<sub>2</sub>) to 4.8 nm (Pt<sub>0.05</sub>Ce<sub>0.475</sub>Zr<sub>0.475</sub>O<sub>2</sub>) with increasing x value, while that of the cubic phase increased from 6.6 nm (Pt<sub>0.05</sub>Ce<sub>0.66</sub>Zr<sub>0.29</sub>O<sub>2</sub>) to 15.2 nm (Pt<sub>0.05</sub>Ce<sub>0.95</sub>O<sub>2</sub>), which can be attributed to the inhibition of crystal growth for mixed oxides. The addition of ZrO<sub>2</sub> into the lattice of CeO<sub>2</sub> lowers the crystallinity of Pt<sub>0.05</sub>Ce<sub>x</sub>Zr<sub>0.95-x</sub>O<sub>2</sub> solid solution.

**Figure 3.** (A) XRD patterns of catalysts and comparison of XRD patterns in (B) 27-32° region and (C) 32-37° region.

Table 1. Textural properties of catalysts measured by XRD and BET analyses.

**BET.** N<sub>2</sub> adsorption-desorption isotherms of all samples are presented in Figure 4. The isotherms of the ZrO<sub>2</sub> and Pt<sub>0.05</sub>Ce<sub>x</sub>Zr<sub>0.95-x</sub>O<sub>2</sub> (x=0, 0.29, 0.475 and 0.66) showed a type IV pattern (IUPAC classification) with a triangular hysteresis loop of type H2 that is typical of materials with mesoscale pore network connectivity. The CeO<sub>2</sub> and Pt<sub>0.05</sub>Ce<sub>0.95</sub>O<sub>2</sub> samples showed typical type II isotherms with H3 hysteresis loop. The pore size distributions of all samples were calculated from the N<sub>2</sub> adsorption isotherms using the BJH analysis. Unlike CeO<sub>2</sub> and Pt<sub>0.05</sub>Ce<sub>0.95</sub>O<sub>2</sub> catalysts, ZrO<sub>2</sub> and Pt<sub>0.05</sub>Ce<sub>x</sub>Zr<sub>0.95-x</sub>O<sub>2</sub> (x=0, 0.29, 0.475 and 0.66) samples showed a narrow distribution.

Table 1 summarizes the BET specific surface area, pore volume, and pore diameter of all catalysts. It can be seen that the surface areas of  $Pt_{0.05}Ce_{0.95}O_2$  and  $Pt_{0.05}Zr_{0.95}O_2$  catalysts were considerably greater compared with those of  $ZrO_2$  or  $CeO_2$  which is consistent with the formation of  $Pt_{0.05}Ce_{0.95}O_2$  and  $Pt_{0.05}Zr_{0.95}O_2$  solid solutions which corroborated the interpretation of the XRD results.

The tensile strain was calculated using Williamson-Hall analysis which relies on the principle that the total peak broadening ( $\beta_{tot}$ ) is sum of size broadening ( $\beta_{size}$ ) and strain broadening ( $\beta_{strain}$ ). Determining the particle size contributions to the line broadening from  $k\lambda/D \cos\theta$  (Scherrer equation) and strain contributions to the line broadening from  $4\epsilon \tan\theta$  [27], we have  $\beta_{tot} \cos\theta = k\lambda/D + 4\epsilon \sin\theta$  in which  $\epsilon$  stands for strain.  $\beta_{tot} \cos\theta$  was plotted with respect to 4 sin $\theta$  and strain is calculated from the slope of the fitted line. The tensile strain for the Pt<sub>0.05</sub>Ce<sub>0.95</sub>O<sub>2</sub> and Pt<sub>0.05</sub>Zr<sub>0.95</sub>O<sub>2</sub> lattices were less than those of ZrO<sub>2</sub> and CeO<sub>2</sub> which has been associated with lower surface energy and hence lower tendency of the crystals to form agglomerates. Pt<sub>0.05</sub>Ce<sub>0.29</sub>Zr<sub>0.66</sub>O<sub>2</sub> and Pt<sub>0.05</sub>Ce<sub>0.95</sub>O<sub>2</sub> catalysts showed the highest and lowest BET specific surface area, respectively. On the other hand, the pore volume increased with increasing Zr content in the cubic and tetragonal structures. Upon Pt addition, pore diameter of CeO<sub>2</sub> and ZrO<sub>2</sub> had decreased about 30%. For Pt<sub>0.05</sub>Ce<sub>x</sub>Zr<sub>0.95-x</sub>O<sub>2</sub> (x=0.29, 0.475 and 0.66) catalysts the average pore diameter decreased with increasing zirconia content.

Figure 4. N<sub>2</sub> physisorption isotherms and corresponding pore size distributions.

**H**<sub>2</sub>-**TPR.** Since the redox characteristics of a catalyst is closely related to its activity, H<sub>2</sub>-TPR was performed to determine the redox behavior of CeO<sub>2</sub>, ZrO<sub>2</sub>, and Pt<sub>0.05</sub>Ce<sub>x</sub>Zr<sub>0.95-x</sub>O<sub>2</sub> samples (Figure 5). The ZrO<sub>2</sub> support showed no reduction peaks up to 800°C, while pure CeO<sub>2</sub> showed one reduction peak at around 560°C which could be assigned to the reduction of surface ceria. There is no evidence of peaks related to reduction of PtO (50°C), PtO<sub>2</sub> (100°C) and with CeO<sub>2</sub> (600°C) in Pt<sub>0.05</sub>Ce<sub>x</sub>Zr<sub>0.95-x</sub>O<sub>2</sub> samples and thus all the observed peaks for Pt<sub>0.05</sub>Ce<sub>x</sub>Zr<sub>0.95-x</sub>O<sub>2</sub> samples are associated with the reduction of mixed oxides [28].

The TPR profile of the Pt-containing CeO<sub>2</sub> and ZrO<sub>2</sub> were significantly modified. For  $Pt_{0.05}Ce_{0.95}O_2$  sample, the presence of a reduction peak at a lower temperature (170°C) suggests that the reduction behavior of CeO<sub>2</sub> was further improved by introducing  $Pt^{2+}$  ions into the ceria lattice leading to higher oxygen mobility and consequently easier bulk reduction of the sample. Similarly,  $Pt_{0.05}Zr_{0.95}O_2$  sample shows a reduction peak at 270°C due to the presence of  $Pt^{4+}$  ions in the zirconia lattice. For  $Pt_{0.05}Ce_xZr_{0.95-x}O_2$  (x=0.29, 0.475 and 0.66) catalysts, reduction peaks were shifted to higher temperatures as compared with the  $Pt_{0.05}Ce_{0.95}O_2$  catalyst.  $Pt_{0.05}Ce_xZr_{0.95-x}O_2$  (x=0.475 and 0.66) catalysts had two reduction peaks at around 170 and 220°C, attributed to introducing  $Pt^{2+}$  and  $Pt^{4+}$  ions into the ceria-zirconia lattice, respectively. The detailed discussion of Pt oxidation state of all samples will be reported in the section dealing with XPS analyses.

With the assumption that the initial Pt oxidation state in the catalyst is  $Pt^{4+}$  (PtO<sub>2</sub>), the nominal hydrogen consumptions and the total hydrogen uptake from TPR are presented in Table 2. For the  $Pt_{0.05}Zr_{0.95}O_2$  catalyst, it can be seen that the nominal hydrogen consumption is quite close to the actual

consumption suggesting that the reduction peak at 270°C is due to the reduction of  $PtO_2$ . On the other hand, for  $Pt_{0.05}Ce_xZr_{0.95-x}O_2$  (x=0.29, 0.475, 0.66 and 0.95) catalysts, the actual hydrogen consumptions were significantly higher compared with nominal values probably due to the reduction of CeO<sub>2</sub>-ZrO<sub>2</sub>. This indicates that the presence of Pt promotes the reduction of ceria via spillover of hydrogen from platinum to the ceria thus shifting the peak for surface ceria reduction to lower temperatures. Also, the reduction peaks of ceria-rich catalysts shifted towards lower temperatures in comparison with the  $Pt_{0.05}Zr_{0.95}O_2$  sample indicating that the reduction of the catalysts strongly depends on the CeO<sub>2</sub> loading. Furthermore, the H<sub>2</sub> consumption increased with increasing ceria content of  $Pt_{0.05}Ce_xZr_{0.95-x}O_2$  solid solutions.

Figure 5. H<sub>2</sub>-TPR profiles of the catalysts.

Table 2. Results obtained by CO chemisorption and H<sub>2</sub>-TPR analyses.

**CO chemisorption.** CO chemisorption results of Pt-containing samples are summarized in Table 2.  $Pt_{0.05}Ce_{0.475}Zr_{0.475}O_2$  and  $Pt_{0.05}Ce_{0.95}O_2$  samples showed the highest and lowest Pt dispersion, respectively, and consequently  $Pt_{0.05}Ce_{0.475}Zr_{0.475}O_2$  had the smallest while  $Pt_{0.05}Ce_{0.95}O_2$  had the largest crystallite size.

**TEM.** The representative TEM images of fresh (as-calcined) catalysts are shown in Figure 6. The particles did not show agglomeration, however, some zones with high and low concentration were observed for the synthesized catalysts. The TEM images suggest that all catalysts exhibited a nanocrystal nature and that the molar ratio of Ce/Zr had a significant effect on the particle size as indicated by the particle size distribution provided for each sample. All catalysts demonstrated a narrow particle size distribution with average particle sizes slightly greater than those calculated from XRD patterns. Furthermore, the lack of evidence of metallic Pt particles in TEM images confirmed the formation of ternary solid solution.

Figure 6. TEM images and corresponding particle size distribution of fresh catalysts.

**Reactivity studies.** An aqueous solution of 10 wt% glycerol was used as feed in catalytic reactor tests performed at 250°C, 50 bar, and WHSV of 2.45 h<sup>-1</sup> for 50 h in a fixed bed reactor. The experimental results are summarized in Table 3. The glycerol conversion over ternary solid solution catalysts was slightly higher than those of Pt-containing CeO<sub>2</sub> and ZrO<sub>2</sub>. Pt<sub>0.05</sub>Ce<sub>0.475</sub>Zr<sub>0.475</sub>O<sub>2</sub> catalyst had the highest activity in APR of glycerol, Pt<sub>0.05</sub>Zr<sub>0.95</sub>O<sub>2</sub> displayed moderate activity, and Pt<sub>0.05</sub>Ce<sub>0.95</sub>O<sub>2</sub> was the least active. The APR activity of Pt catalysts has been correlated with their WGS activity since efficient CO removal from the catalyst surface is important at the relatively low reaction temperatures

employed under APR conditions [16,29-31]. One explanation for this observation is that improved surface oxygen mobility could enhance the rate of WGS reaction. The high APR activity observed in  $Pt_{0.05}Ce_xZr_{0.95-x}O_2$  catalysts could therefore be explained by considering that introducing the more electronegative Zr atoms (compared with Ce atoms) in the ceria lattice could induce significant lattice distortions thus increasing both the oxygen mobility and the concentration of oxygen vacancies in the lattice [16,17,32] as was also evidenced by the H<sub>2</sub>-TPR (Figure 5) and XPS (Figure 8) results. Another possible explanation for the high APR activity of  $Pt_{0.05}Ce_xZr_{0.95-x}O_2$  catalysts could be their resistance to the negative effect of  $CO_2$  re-adsorption that could lead to the formation of various carbonate species.  $Pt_{0.05}Ce_xZr_{0.95-x}O_2$  catalysts are less sensitive to irreversible deactivation by  $CO_2$  compared with  $Pt_{0.05}Zr_{0.95}O_2$  and  $Pt_{0.05}Ce_{0.95}O_2$  catalysts [33].

Ternary solid solution catalysts produced higher hydrogen yield, carbon conversion to gas, and hydrogen selectivity than binary ones except in the case of  $Pt_{0.05}Ce_{0.66}Zr_{0.29}O_2$ . For most of the catalysts, the total H<sub>2</sub> yields were lower than what was expected in terms of the stoichiometric ratio of H<sub>2</sub> to CO<sub>2</sub> in the overall reforming reaction (=7/3). This was due to the H<sub>2</sub> consumption in the hydrogenation of dehydrated reaction intermediates. The large H<sub>2</sub>/CO<sub>2</sub> ratio of Pt<sub>0.05</sub>Ce<sub>0.95</sub>O<sub>2</sub> was an exception that was due to the low hydrogenation activity of this catalyst. The lowest H<sub>2</sub> selectivity and yield, as well as carbon conversion to gas was achieved by Pt<sub>0.05</sub>Ce<sub>0.95</sub>O<sub>2</sub> which could be explained by its low surface area and metal dispersion (Tables 1 and 2). Additionally, in the absence of Zr, interactions between the CeO<sub>2</sub> and Pt could be induced thus enhancing the oxidation of Pt [34] that would consequently lead to a less active metal surface [35].

The product gas distributions from the catalytic reactor tests are presented in Table 3. H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> were the only gaseous products. No CO was detected in the product gases indicating that the CO concentrations were below the GC detection limit (i.e., <100 ppm). Pt<sub>0.05</sub>Ce<sub>0.475</sub>Zr<sub>0.475</sub>O<sub>2</sub> and Pt<sub>0.05</sub>Ce<sub>0.29</sub>Zr<sub>0.66</sub>O<sub>2</sub> catalysts led to H<sub>2</sub>-rich product gas streams containing 70 and 69 mol% H<sub>2</sub>, respectively. The fraction of H<sub>2</sub> in the product gases was strongly correlated with the active metal surface area of the catalyst (Table 2) confirming the important effect of particle size on catalyst performance. The gas product from APR over Pt<sub>0.05</sub>Ce<sub>0.475</sub>Zr<sub>0.475</sub>O<sub>2</sub> catalyst contained less CH<sub>4</sub> indicating a lower rate for methanation reaction. This catalyst also had the highest normalized rate of H<sub>2</sub> production, 65 cm<sup>3</sup> g<sub>cat</sub><sup>-1</sup> min<sup>-1</sup>. H<sub>2</sub> production rate increased with increasing Pt dispersion as shown in Tables 2 and 3. Low Pt dispersion, and consequently large particle size, favored the methanation reaction.

**Table 3.** Performance of catalysts in APR of 10 wt% glycerol under conditions of 250°C, 50 bar and WHSV of 2.45  $h^{-1}$  for 50 h in a fixed bed reactor.

Contribution of this work with respect to the work of other researchers are summarized in Table 4. Comparison between Table 3 and Table 4 shows higher H<sub>2</sub> yield and H<sub>2</sub> selectivity of present catalysts. H<sub>2</sub> production rate in terms of cm<sup>3</sup>  $g_{cat}^{-1}$  min<sup>-1</sup> for Pt<sub>0.05</sub>Ce<sub>x</sub>Zr<sub>0.95-x</sub>O<sub>2</sub> solid solutions is 3 times higher than those reported by Jeon and co-workers [36] for Pt/CeO<sub>2</sub>-ZrO<sub>2</sub> hetero-structures in which Pt was impregnated on CeO<sub>2</sub>-ZrO<sub>2</sub> supports. Turnover frequency (TOF) of our solid solutions in the present study were 18 times higher than those for hetero-structures reported by Ciftci and co-workers [37].

Table 4. Results of APR of glycerol under different experimental conditions

The reactor test results clearly indicated the advantage of ternary solid solution catalysts in the Ptcatalyzed APR. Zr addition to Ce resulted in a significant increase in the active metal surface area of the Pt catalysts (Table 2) which consequently resulted in improved H<sub>2</sub> yield, H<sub>2</sub> selectivity, CH<sub>4</sub> selectivity, and carbon to gas conversion such that each additional  $m^2g^{-1}$  of active metal surface area resulted in an approximate increase of 5.2% in the yield of H<sub>2</sub>, 2.5% increase in selectivity of H<sub>2</sub>, 3.2% increase in carbon to gas conversion as well as 2.5% decrease in CH<sub>4</sub> formation [Figure 7(A)]. Moreover, the addition of Zr to Ce (up to 47.5 wt% of Zr in Pt<sub>0.05</sub>Ce<sub>x</sub>Zr<sub>0.95-x</sub>O<sub>2</sub> structure) resulted in the formation of smaller particles which in turn led to improved catalytic performance [Figure 7(B)] suggesting that the particle size of the catalyst might be one of the most important controlling factors for aqueous phase reforming. Among the catalysts tested, Pt<sub>0.05</sub>Ce<sub>0.475</sub>Zr<sub>0.475</sub>O<sub>2</sub> showed the best catalytic performance which may be attributed to the highest Pt dispersion and the synergistic effect of smallest particle size and large pore diameter (Tables 1 and 2) that was also consistent with higher active metal surface area measured from CO-chemisorption (Table 2). These along with the XPS results to follow could account for the favorable performance of this catalyst.

An inverse dependence of the TOF and metal dispersion on active metal surface area [Figure 7(C)] and average particle size [Figure 7(D)] is observed, indicating that APR of glycerol is a structuresensitive reaction, i.e. adsorption and C–C cleavage of polyols preferably occurred on the face Pt atoms rather than on edge and corner atoms. As the particle size increases, the number of face atoms increases whereas the number of corner and edge atoms decrease [38]. Therefore, assuming that face Pt atoms are much more active in APR than edge and corner atoms, the TOF should increase with an increase of the average particle size. The results regarding the TOF dependence on the average particle size and active metal surface area are in very good agreement with the results reported by other investigators [39,40].

**Figure 7.** Correlation between the results of aqueous phase reforming and (A, C) active metal (Pt) surface area and (B, D) particle size. Aqueous phase reforming was performed using 0.05 mL  $h^{-1}$  of 10 wt% aqueous glycerol as the feedstock (250 °C, 50 bar, 250 mg catalyst) with data averaged over 50 h of reaction.

**XPS.** In order to see if the solid solution is itself the catalytically active phase and Pt is not extruded from the solid solution under the redox conditions of APR reaction, XPS measurements were performed to determine the chemical state of platinum in the nano-catalysts. XPS spectra of the Pt(4f) core level region in fresh (as-calcined) and used (after APR of 10 wt% glycerol under conditions of 250°C, 50 bar and WHSV of 2.45 h<sup>-1</sup> for 50 h in a fixed bed reactor) catalysts are presented in Figure 8. All samples exhibited two broad energy bands corresponding to the Pt  $4f_{7/2}$  (at lower binding energies) and Pt  $4f_{5/2}$  (at higher binding energies) core electrons, whose position strongly depended on the Zr/Ce ratio. The binding energies of the Pt  $4f_{7/2}$  and Pt  $4f_{5/2}$  core electrons shifted toward higher values as the Zr content of the sample increased as a result of the replacement of the less electronegative Ce by the more electronegative Zr in the solid solution. The increase of the binding energies of Pt 4f electrons may be ascribed to the electronic interactions between the Pt, Ce and/or Zr atomic orbitals, leading to partial electron transfer from Pt to Ce and Zr. Such variation of the binding energy has also been reported for other Pt-based bi-metallic nano-particles [41,42].

According to what is explained above, in the samples with greater Zr content, Pt has become relatively poor in electron density. Such electron withdrawing from Pt would result in moderating the strength of the Pt-CO bonds formed during APR reaction subsequently leading to an enhancement in WGS reaction and a more facile removal of surface adsorbed intermediates [43] thus increasing the APR reaction activity. In addition, the intensity of the Pt 4f peaks of the samples strongly depended on the surface content of Pt as determined by CO chemisorption (Table 2). Considering the full width at half maximum and  $4f_{(7/2,5/2)}$  spin-orbit splitting value, Pt ( $4f_{7/2,5/2}$ ) peaks in all samples were deconvoluted into only two sets of spin-orbit doublets which could be assigned to  $Pt^{2+}$  and  $Pt^{4+}$ . This observation agrees well with the XRD and TEM results. Moreover, Pt has a multiple oxidation state which is determined by the extent of defects formation in the final crystallized sample. Crystallization of ZrO<sub>2</sub> results in Zr in +4 oxidation state and with zirconia being highly irreducible, Pt can be substituted in the Zr lattice in +4 oxidation state without any defect formation and thus Pt remains mainly in +4 state in the  $Pt_{0.05}Zr_{0.95}O_2$  sample. Conversely, Pt in +2 state was dominant in  $Pt_{0.05}Ce_{0.95}O_2$ sample because both +3 and +4 oxidation states exist for Ce thus increasing the possibility of defect formation in the case of  $Pt_{0.05}Ce_{0.95}O_2$ . In  $Pt_{0.05}Ce_xZr_{0.95-x}O_2$  (x=0.29, 0.475 and 0.66) catalysts the proportion of Pt in +4 state increased with increasing Zr content.

Analysis of the spent catalysts after APR reaction indicated no significant changes in the oxidation state of Pt or in the peak intensities. Ceria has high potential to facilitate the oxidization of Pt and stabilizing it in its' oxidized state because of the higher redox potential of the  $Ce^{4+}/Ce^{3+}$  couple (1.61 eV) compared with those of the  $Pt^{2+}/Pt^0$  (1.19 eV) and  $Pt^{4+}/Pt^{2+}$  (1.05 eV) couples [44]. The introduction of Pt into ceria–zirconia solid solution instead of impregnating Pt on ceria–zirconia mixed oxide support, appears to be capable of stabilizing Pt in its' oxide form against the APR redox conditions.

This is an important observation since it is well known that Pt segregates out from the Pt impregnated ceria-zirconia catalysts under APR conditions [6,35,45].

Figure 8. High-resolution XPS spectra of Pt 4f region of fresh and spent catalysts.

**Stability studies.** The catalyst stability was evaluated in terms of the hydrogen yield [Figure 9(A)]. The catalytic performance remained constant during at least 50 h of the APR reaction of 10 wt% glycerol under conditions of 250°C, 50 bar, and WHSV of 2.45 h<sup>-1</sup> indicating that the catalysts had excellent stability without any degradation as was also evident from XPS analysis. The representative TEM images and particle size distribution of the spent catalysts are shown in Figure 10. No evidence of agglomeration was observed for the spent catalysts which had similar narrow size distributions and average particle sizes close to those of the fresh samples. This was also confirmed by both XPS and TEM results of the spent samples.

The  $Pt_{0.05}Ce_{0.475}Zr_{0.475}O_2$  catalyst, which resulted in the highest H<sub>2</sub> yield from the APR of glycerol in the catalyst screening studies, was used to investigate the effects of WHSV on the reaction activities at fixed catalyst loading (250 mg). Figure 9(B) presents the results from APR of glycerol solutions with six different WHSV (0.12, 0.6, 1.2, 1.8, 2.4, 3 and 3.6 h<sup>-1</sup>). The APR of glycerol at WHSV=2.4 h<sup>-1</sup> produced a significantly higher H<sub>2</sub> yield than other WHSV values tested. At WHSV>2.4 h<sup>-1</sup> methanation was mitigated and the WGS reaction was favored. At WHSVs less than or equal to 2.4 h<sup>-1</sup>, sufficient contact between the glycerol reactant and the catalyst allowed the reforming reaction to take place; the shorter contact time (i.e., for WHSV>2.4 h<sup>-1</sup>) only resulted in partial conversion of glycerol. The stability of  $Pt_{0.05}Ce_{0.475}Zr_{0.475}O_2$  catalyst was investigated by changing WHSV from 0.12 to 3.6 h<sup>-1</sup> [Figure 9(C)]. This catalyst had excellent stability in all examined WHSV values during 50 h of the APR reaction.

**Figure 9.** (A) Performance of catalysts during 50 h of continuous APR reaction using 10 wt% glycerol and WHSV of 2.45 h<sup>-1</sup>, (B) The effect of the WHSV on H<sub>2</sub> yield APR over  $Pt_{0.05}Ce_{0.475}Zr_{0.475}O_2$  and (C) Performance of  $Pt_{0.05}Ce_{0.475}Zr_{0.475}O_2$  during 50 h of continuous APR reaction using various WHSV. All reactions conducted using 250 °C, 50 bar and 250 mg catalyst.

Figure 10. TEM image and corresponding particle size distribution of spent catalysts.

#### Conclusions

Glycerol can be converted into  $H_2$ -rich gas over Pt catalysts. Reactivity and characteristic measurements on  $Pt_{0.05}Ce_xZr_{0.95-x}O_2$  with varying compositions of Zr and Ce revealed notable

differences in the catalytic activities and product distributions from the APR reaction. Ternary solid solution catalysts showed remarkably enhanced catalytic performance towards the APR of glycerol. Of these catalysts,  $Pt_{0.05}Ce_{0.475}Zr_{0.475}O_2$  with high Pt dispersion and small particle size, along with the large pore diameter and high active metal surface area was found to be very active and stable in APR of glycerol, had the highest carbon to gas conversion (95%), highest H<sub>2</sub> yield (93%), highest H<sub>2</sub> selectivity (98%) and at least 50 h of stability. Achieving a highly active and stable catalyst for the aqueous phase reforming of glycerol was the focus of our current investigation.

#### References

- [1] S. Dunn, Int. J. Hydrogen Energy 27 (2002) 235-264.
- [2] R. D. Cortright, R. R. Davda, J. A. Dumesic, Nature 418 (2002) 964-967.
- [3] G. W. Huber, J. A. Dumesic, Catal. Today 111 (2006) 119-132.
- [4] R. R. Davda, J. W. Shabaker, G. W. Huber, R. D. Cortright, J. A. Dumesic, Appl. Catal. B 56 (2005) 171-186.
- [5] R. R. Davda, J. A. Dumesic, Chem. Commun. (2004) 36-37.
- [6] J. W. Shabaker, G. W. Huber, R. R. Davda, R. D. Cortright, J. A. Dumesic, Catal. Lett. 88 (2003) 1-8.
- [7] J. W. Shabaker, R. R. Davda, G. W. Huber, R. D. Cortright, J. A. Dumesic, J. Catal. 215 (2003) 344-352.
- [8] G. W. Huber, J. W. Shabaker, S. T. Evans, J. A. Dumesic, Appl. Catal., B 62 (2006) 226-235.
- [9] R. L. Manfro, A. F. da Costa, N. F. P. Riberio, M. M. V. M. Souza, Fuel Process. Technol. 92 (2011) 330-335.
- [10] J. W. Shabaker, G. W. Huber, J. A. Dumesic, J. Catal. 222 (2004) 180-191.
- [11] G. Wen, Y. Xu, H. Ma, Z. Xu, Z. Tian, Int. J. Hydrogen Energy 33 (2008) 6657-6666.
- [12] A. Ciftci, B. Peng, A. Jentys, J. A. Lercher, E. J. M. Hensen, Appl. Catal., A 431 (2012) 113-119.
- [13] K. Koichumanova, A. K. K. Vikla, D. J. M. de Vlieger, K. Seshan, B. L. Mojet, L. Lefferts, ChemSusChem 6 (2013) 1717-1723.
- [14] G. Wen, Y. Xu, Z. Xu, Z. Tian, Catal. Lett. 129 (2009) 250-257.
- [15] C. M. Kalamaras, D. D. Dionysiou, A. M. Efstathiou, ACS Catal. 2 (2012) 2729-2742.
- [16] C. I. Vignatti, M. S. Avila, C. R. Apesteguia, T. F. Garetto, Catal. Today 171 (2011) 297-303.
- [17] Y. T. Kim, S. J. You, E. D. Park, Int. J. Hydrogen Energy 37 (2012) 1465-1474.
- [18] H. S. Roh, H. S. Potdar, K. W. Jun, S. W. Han, J. W. Kim, Catal. Lett. 93 (2004) 203-207.
- [19] J. L. Ayastuy, M. P. Gonzalez-Marcos, A. Gil-Rodriguez, J. R. Gonzalez-Velasco, M. A. Gutierrez-Ortiz, Catal. Today 116 (2006) 391-399.
- [20] M. M. Rahman, T. L. Church, A. I. Minett, A. T. Harris, ChemSusChem 6 (2013) 1006-1013.
- [21] M. L. Barbelli, F. Pompeo, G. F. Santori, N. N. Nichio, Catal. Today 213 (2013) 58-64.
- [22] A. O. Menezes, M. T. Rodrigues, A. Zimmaro, L. E. P. Borges, M. A. Fraga, Renewable Energy 36 (2011) 595-599.
- [23] Y. Guo, M. U. Azmat, X. Liu, Y. Wang, G. Lu, Appl. Energy 92 (2012) 218-223.
- [24] A. Wawrzetz, B. Peng, A. Hrabar, A. Jentys, A. A. Lemonidou, J. A. Lercher, J. Catal. 269 (2010) 411-420.
- [25] M. El Doukkali, A. Iriondo, J. F. Cambra, L. Jalowiecki-Duhamel, A. S. Mamede, F. Dumeignil, P. L. Arias, J. Mol. Catal. A: Chem. 368 (2013) 125-136.
- [26] V. Dal Santo, A. Gallo, A. Naldoni, M. Guidotti, R. Psaro, Catal. Today 197 (2012) 190-205.
- [27] Y. T. Prabhu, K. V. Rao, V. S. S. Kumar, B. S. Kumari, World J. Nano Sci. Eng. 4 (2012) 21-28.

- [28] P. Fornasiero, J. Kaspar, T. Montini, M. Graziani, V. Dal Santo, R. Psaro, S. Recchia, J. Mol. Catal. A: Chem. 204-205 (2003) 683-691.
- [29] A. Ciftci, D. A. J. M. Ligthart, A. O. Sen, A. J. F. van Hoof, H. Friedrich, E. J. M. Hensen, J. Catal. 311 (2014) 88-101.
- [30] E. L. Kunkes, D. A. Simonetti, J. A. Dumesic, W. D. Pyrz, L. E. Murillo, J. G. Chen, D. J. Buttrey, J. Catal. 260 (2008) 164-177.
- [31] D. A. Simonetti, E. L. Kunkes, J. A. Dumesic, J. Catal. 247 (2007) 298-306.
- [32] S. Ricote, G. Jacobs, M. Milling, Y. Ji, P. M. Patterson, B. H. Davis, Appl. Catal. A 303 (2006) 35-47.
- [33] M. W. Balakos, M. R. Madden, T. L. Walsh, J. P. Wagner, Proceedings of the AIChE Spring National Meeting, New Orleans, LA, 2004.
- [34] Q. Zhuang, Y. Qin, L. Chang, Appl. Catal. 70 (1991) 1-8.
- [35] Y. F. Y. Yao, Ind. Eng. Chem. Prod. Res. Dev. 19 (1980) 293-298.
- [36] S. Jeon, H. Ham, Y. Suh, J. W. Bae, RSC Adv. 5 (2015) 54806-54815.
- [37] A. Ciftci, S. Eren, D. A. J. M. Ligthart, E. J. M. Hensen, ChemCatChem 6 (2014) 1260-1269.
- [38] A. V. Kirilin, B. Hasse, A. V. Tokarev, L. M. Kustov, G. N. Baeva, G. O. Bragina, A. Y. Stakheev, A. Rautio, T. Salmi, B. J. M. Etzold, J. Mikkolaae, D. Y. Murzin, Catal. Sci. Technol. 4 (2014) 387-401.
- [39] K. Lehnert, P. Claus, Catal. Commun. 9 (2008) 2543-2546.
- [40] T. Kim, H. Kim, K. Jeong, H. Chae, S. Jeong, C. Lee, C. Kim, Green Chem. 13 (2011) 1718-1728.
- [41] J. B. Xu, T. S. Zhao, Z. X. Liang, J. Phys. Chem. C 112 (2008) 17362-17367.
- [42] J. H. Zeng, J. Yang, J. Y. Lee, W. J. Zhou, J. Phys. Chem. B 110 (2006) 24606-24611.
- [43] K. W. Park, J. H. Choi, B. K. Kwon, S. A. Lee, Y. E. Sung, H. Y. Ha, S. A. Hong, H. Kim, A. Wieckowski, J. Phys. Chem. B 106 (2002) 1869-1877.
- [44] J.A. Dean, Lange's Handbook of Chemistry, fifteenth ed., McGraw-Hill, New York, 1998.
- [45] H. J. Park, H. D. Kim, T. W. Kim, K. E. Jeong, H. J. Chae, S. Y. Jeong, Y. M. Chung, Y. K. Park, C. U. Kim, ChemSusChem 5 (2012) 629-633.

	XRD			BET					
		Crystallite size (nm) <sup>a</sup>		Lattice parameter (Å) <sup>b</sup>			BET surface	Pore volume	Pore diameter
Catalyst	Lattice type	cubic	tetragonal	α = β	Y	Crystallinity (%)	area (m² g⁻¹)	(cm <sup>3</sup> g <sup>-1</sup> )	(nm)
CeO <sub>2</sub>	cubic	15.1	-	5.42	5.42	74	13	0.06	18
Pt <sub>0.5</sub> Ce <sub>0.95</sub> O <sub>2</sub>	cubic	15.2	-	5.41	5.41	66	38	0.12	12
Pt <sub>0.5</sub> Ce <sub>0.66</sub> Zr <sub>0.29</sub> O <sub>2</sub>	cubic	6.6	-	5.38	5.38	53	91	0.15	7
Pt <sub>0.5</sub> Ce <sub>0.475</sub> Zr <sub>0.475</sub> O <sub>2</sub>	tetragonal	-	4.8	3.73	5.27	48	81	0.13	6
Pt <sub>0.5</sub> Ce <sub>0.29</sub> Zr <sub>0.66</sub> O <sub>2</sub>	tetragonal	-	5.2	3.67	5.22	40	102	0.13	5
Pt <sub>0.5</sub> Zr <sub>0.95</sub> O <sub>2</sub>	tetragonal	-	9.2	3.61	5.09	40	101	0.17	7
ZrO <sub>2</sub>	tetragonal	-	11.7	3.62	5.12	31	64	0.16	10

<sup>a</sup> Crystallite size is obtained from Scherrer's equation. <sup>b</sup> Lattice parameter is obtained from Bragg's Law.

	CO chemisorption	ו	H <sub>2</sub> -TPR			
Catalyst	CO uptake (µmol CO g <sub>cat</sub> -1)	Mean particle size (nm) <sup>a</sup>	Pt surface area $(m^2 g_{cat}^{-1})^b$	Pt dispersion (%) <sup>C</sup>	$H_2$ consumption (mmol $H_2 g_{cat}^{-1}$ )	Nominal H <sub>2</sub> consumption (mmol H <sub>2</sub> $g_{cat}^{-1}$ )
CeO <sub>2</sub>	-	-	-	-	1.3	0.51
Pt <sub>0.5</sub> Ce <sub>0.95</sub> O <sub>2</sub>	21	13.9	1	8	1.5	0.51
Pt <sub>0.5</sub> Ce <sub>0.66</sub> Zr <sub>0.29</sub> O <sub>2</sub>	38	7.6	2	15	2.1	0.51
Pt <sub>0.5</sub> Ce <sub>0.475</sub> Zr <sub>0.475</sub> O <sub>2</sub>	101	2.9	5	39	1.7	0.51
Pt <sub>0.5</sub> Ce <sub>0.29</sub> Zr <sub>0.66</sub> O <sub>2</sub>	90	3.2	4	35	1.2	0.51
Pt <sub>0.5</sub> Zr <sub>0.95</sub> O <sub>2</sub>	49	6	2	19	0.5	0.51
ZrO.	_	_	_	_	03	0.51

	Glycerol conversion (%) <sup>a</sup>	Carbon to gas conversion (%) <sup>b</sup>	$H_2$ yield (%) <sup>c</sup>	Selectivity (%)		Gas product (mol %)			H <sub>2</sub> production rate		
Catalyst				$H_2^d$	CH₄ <sup>e</sup>	H <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	(cm <sup>3</sup> g <sub>cat</sub> <sup>-1</sup> min <sup>-1</sup> )	IOF (min )	
Pt <sub>0.5</sub> Ce <sub>0.95</sub> O <sub>2</sub>	99.2	81	71	87	13	67	29	4	49	105	
Pt <sub>0.5</sub> Ce <sub>0.66</sub> Zr <sub>0.29</sub> O <sub>2</sub>	99.4	87	78	89	8	67	30	3	54	64	
Pt <sub>0.5</sub> Ce <sub>0.475</sub> Zr <sub>0.475</sub> O <sub>2</sub>	99.8	95	93	98	2	70	30	0	65	29	
Pt <sub>0.5</sub> Ce <sub>0.29</sub> Zr <sub>0.66</sub> O <sub>2</sub>	99.5	93	89	95	3	69	30	1	62	31	
$Pt_0 = Zr_0 = O_2$	99.3	91	85	93	5	68	30	2	59	55	

a Glycerol conversion=amount of glycerol removed from liquid phase/amount of glycerol in feedstock\*100

<sup>b</sup> Carbon to gas conversion=number of C atoms in gas product/number of C atoms fed into the reactor\*100

Carbon to gas conversion=number of C atoms in gas product number of C atoms to the factor  $^{c}$  H<sub>2</sub> yield= H<sub>2</sub> produced experimentally/7/glycerol molar flow rate fed into the reactor\*100  $^{d}$  H<sub>2</sub> selectivity=2\*H<sub>2</sub> produced experimentally/total number of H atoms in gas product\*100  $^{e}$  CH<sub>4</sub> selectivity=CH<sub>4</sub> produced experimentally/total number of C atoms in gas product\*100  $^{e}$  CH<sub>4</sub> selectivity=CH<sub>4</sub> produced experimentally/total number of C atoms in gas product\*100  $^{e}$ 

<sup>t</sup> TOF= H<sub>2</sub> production rate/moles of chemisorped CO\*Stoichiometry factor (in this case=1)

	Re	eaction conditions					
Catalyst	Temperature (°C)	Pressure (bar)	Glycerol wt%	H <sub>2</sub> yield (%) <sup>a</sup>	H <sub>2</sub> Selectivity (%) <sup>D</sup>	Reactor type	Ref.
3 wt% Pt/3 wt% CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	220	30	5	56	88	fixed-bed	20
1.1 wt% Pt/4 wt% CeO <sub>2</sub> /1 wt% ZrO <sub>2</sub> /α-Al <sub>2</sub> O <sub>3</sub>	250	44	10	20	81	batch	21
1.49 wt% Pt/CeO <sub>2</sub>	225	23	1	27	-	batch	22
0.75 wt% Pt/CeO <sub>2</sub>	225	27.6	5	21.4	58.9	fixed-bed	23
5 wt% Pt/CeO <sub>2</sub> -ZrO <sub>2</sub> (Ce/Ce+Zr=0.4)	250	45	10	8.5	74.3	fixed-bed	35
2.76 wt% Pt/Ce <sub>0.25</sub> Zr <sub>0.75</sub> O <sub>2</sub>	225	25	10	26.5	-	autoclave	36

<sup>a</sup>  $H_2$  yield=  $H_2$  produced experimentally/ $H_2$  produced theoretically\*100 <sup>b</sup>  $H_2$  selectivity=2\* $H_2$  produced experimentally/total number of H atoms in gas product\*100











Intensity (a. u.)









