



Effect of the Preparation Method of Support on the Aqueous Phase Reforming of Ethylene Glycol Over 2 wt% Pt/Ce_{0.15}Zr_{0.85}O₂ Catalysts

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The effect of catalyst support on the aqueous phase reforming of ethylene glycol over supported 2 wt% Pt/Ce_{0.15}Zr_{0.85}O₂ catalysts have been investigated. Various types of Ce_{0.15}Zr_{0.85}O₂ mixed oxides were prepared by hydrothermal precipitation (CZH), modified precipitation (CZM), co-precipitation (CZC), sol-gel (CZS) methods, respectively. Catalysts were characterized by XRD, N₂ sorption analysis, and cyclohexane dehydration for relative metal dispersion. The support effect on the activity of 2 wt% Pt/Ce_{0.15}Zr_{0.85}O₂ catalysts with different preparation method was given as follows: CZH < CZM < CZC < CZS. Pt/Ce_{0.15}Zr_{0.85}O₂ (CZS) catalyst showed good catalytic activity for APR reaction due to its high metal dispersion and reducibility. The effect of reaction conditions such as reaction temperature, weight hourly space velocity (WHSV) was also studied. The hydrogen production rate and hydrogen yield increased in proportion to the reaction temperature and corresponding system pressure, whereas WHSV did not affect.

Keywords: Aqueous Phase Reforming, Pt Catalyst, Ceria-Zirconia, Hydrogen Yield, Ethylene Glycol.

1. INTRODUCTION

Researchers are currently developing ways to utilize renewable resources as a feedstock for energy generation and chemical production, with the aim of reducing CO₂ emissions as well as the dependency on fossil fuels. Among these efforts, hydrogen production has been attracting considerable attention.¹ Recently, an aqueous phase reforming (APR) process has drawn the attention in specific application fields like production of hydrogen from oxygenated hydrocarbons (e.g., ethylene glycol, glycerol, sorbitol).² Ethylene glycol is a particularly relevant feed molecule for studies of aqueous-phase reforming reactions because it contains the same functionalities of larger polyols, including C—C, C—O, C—H, and O—H bonds, and also OH groups on adjacent carbon atoms.³

The nature of the support would have remarkable influence on the activity as well as the gas distribution of the products. In supported metal catalyst, the support not only modifies the metal dispersion, but there are also metal-support interactions due to physical and chemical

properties of both. Until now, various supports were applied in this APR studies such as carbonaceous material, metal oxide etc.^{3–5} It was reported that the supported Pt catalysts can be ranked in the following order with respect to the rate of hydrogen production: TiO₂ > Al₂O₃; carbon; Pt-black > SiO₂–Al₂O₃, ZrO₂ > CeO₂, ZnO, SiO₂.³ On the contrary, it was found that the overall activities for APR of glycerol decreased in the following order: Pt/MgO > Pt/Al₂O₃ > Pt/CeO₂ > Pt/TiO₂ > Pt/SiO₂ and suggested that the basic sites are prefer for water-gas shift and further enhanced the APR process.⁴

The solid solution of ceria and zirconia-containing composite was of great significance and hold intensive interest for researchers because of their successful applications as automotive three-way catalysts (TWCs), as well as ultraviolet (UV) absorbers, solid oxide fuel cells (SOFCs).^{6,7} It was found that its unique redox properties CeO₂ catalyzes the conversion of CO and promotes the water-gas shift and the steam-reforming reactions.^{6–8} However, the properties of these materials largely depend on the preparation methods. So far, many synthesis methods of ceria-zirconia mixture has been reported by various methods such as co-precipitation,⁹ urea combustion,¹⁰

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hydrothermal,¹¹ sol–gel synthesis,¹² surfactant assistant method¹³ and others. Therefore, investigating the effects of preparation methods on the properties of Ce_xZr_{1-x}O₂ solid solutions is critical for developing rare earth oxygen storage and catalyst materials.¹⁴

In this work, we have studied the effects of the support on the activity and selectivity of Pt-based Ce_{0.15}Zr_{0.85}O₂ catalysts for APR of ethylene glycol. Ce/Zr mixed oxides composition was chosen in our previous study with optimal activity on different composition of Ce/Zr as APR catalyst. Until now, there is no open literature focusing on the investigation of the support preparation process on the APR of polyol such as ethylene glycol. Four types of Ce_{0.15}Zr_{0.85}O₂ mixed oxides were prepared by hydrothermal synthesis (CZH), modified precipitation (CZM), co-precipitation (CZC), and sol–gel (CZS) methods, respectively.

The interaction of Pt active material and Ce_{0.15}Zr_{0.85}O₂ support for catalytic activity and selectivity was discussed in detail.

2. EXPERIMENTAL DETAILS

2.1. Synthesis of Ce_{0.15}Zr_{0.85}O₂ Support

2.1.1. Co-Precipitation (CZC)

Ce_{0.15}Zr_{0.85}O₂ was prepared via co-precipitation of Ce(NO₃)₃ and ZrO(NO₃)₂ according to literature.⁹ The solution of aqueous NH₃ was dropped into the mixed salt solution under continuous stirring and the pH value was controlled to be 10. After aging at room temperature for 24 h, the precipitate was filtered and washed with deionized water until no pH change could be detected. Then the precipitate was dried at room temperature overnight. Finally, the precipitate was calcined in air 500 °C for 2 h.

2.1.2. Sol–Gel Method (CZS)

Sol–gel method was applied to prepare Ce_xZr_{1-x}O₂ solid solutions. Citric acid and Ethylene glycol solution was added into Ce(NO₃)₃ and Zr(NO₃)₂ solution, respectively. Each Ceria and Zirconia solution was mixed at 60 °C for 30 min. Mixture was stirred with elevating temperature from 60 °C to 200 °C until it transformed into a yellow gel, and then the gel was dried at 100 °C for overnight, followed by stepwise calcinations at various temperatures of 100, 200, 300, 400, and 500 °C for 2 h, respectively.¹²

2.1.3. Hydrothermal Precipitation (CZH)

Ce_{0.15}Zr_{0.85}O₂ was prepared by adding the cationic surfactant (cetyltrimethylammonium bromide (CTAB)) to the mixed solution of Ce(NO₃)₃ and Zr(NO₃)₂ precursor with ethanol. The solution of aqueous ammonia was added to the above mixed solution under vigorous agitation.

The molar ratio of Ce/Zr was 15/85 and (Ce + Zr)/CTAB was kept to 1.0. The pH value of the mixture was adjusted to 10. Then the slurry was sealed in a teflon-lined stainless autoclave and hydrothermally treated at 100 °C for 1 h. The precipitate was separated by filtration, washed with deionized water until no pH change could be detected, and dried at 110 °C for 2 h. Finally, the precipitate was calcined in air 500 °C for 2 h.¹¹

2.1.4. Modified Precipitation (CZM)

Modified precipitation method was similar to co-precipitation except that urea was added to the Ce(NO₃)₃ and ZrO(NO₃)₂ solution.¹⁴

2.2. Catalyst Preparation

2 wt% Pt/Ce_{0.15}Zr_{0.85}O₂ catalysts using four different supports were prepared by wet impregnation method with aqueous solution of H₂PtCl₆ · 6H₂O (Acros, 99.9%) using rotary evaporator. After impregnation, the samples were dried at 100 °C, 1 h and then calcined at 500 °C for 2 h. These as-prepared fresh catalysts were denoted as 2 wt% Pt/CZH, 2 wt% Pt/CZM, 2 wt% Pt/CZC and 2 wt% Pt/CZS, respectively.

2.3. Characterizations

All the catalysts were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), N₂-sorption, and temperature programmed reduction (TPR). Cyclohexane dehydrogenation was used to estimate platinum dispersion according to literature.¹⁵ Since H₂ and CO adsorption occurs concurrently over CeO₂ support, cyclohexane dehydrogenation was employed.

2.4. Catalytic Test

Aqueous phase reforming of 10 wt% ethylene glycol was performed in a lab made fixed bed reactor system according to our previous studies.¹⁶ A liquid feed of 10 wt% ethylene glycol in deionized water was fed into the catalytic reactor at 0.1 ml/min. Before performing an aqueous phase reforming reaction, the catalyst goes through H₂ reduction step in 50 mL/min flow at 260 °C (heating rate of 1.0 °C/min) for 2 h. This reforming reaction was performed with 2.0 h⁻¹ of weight hourly space velocity (WHSV) at 250 °C under 45 atm. The effluent gas products were measured by a gas chromatograph.

3. RESULTS AND DISCUSSION

3.1. Characterization of Supports and Catalysts

The XRD patterns of the ceria-zirconia (CZ) supported Pt catalysts are presented in Figure 1. All samples

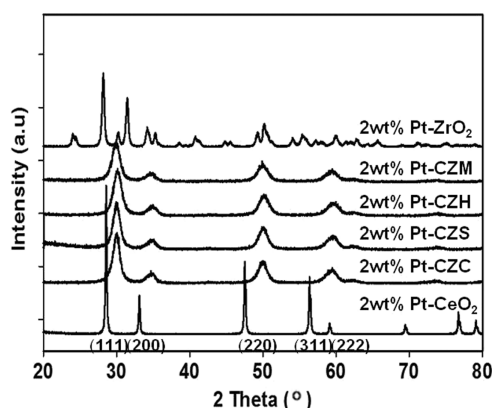


Fig. 1. XRD patterns of the 2 wt% Pt/Ce_{0.15}Zr_{0.85}O₂ catalysts.

exhibit only peaks which could refer to a typical cubic fluorite structure. The major peaks of all samples are corresponding to the (111), (200), (220), (311) and (222) crystallographic planes, which indicate the formation of CeO₂-ZrO₂ solid solutions. But these peaks displayed a small shift to higher values of 2θ , as compared to cubic fluorite CeO₂. It is associated with lattice contraction caused by the introduction of smaller Zr⁴⁺ ions in the CeO₂ lattice.¹⁷ The structure of ceria-zirconia (CZ) supports and Pt catalysts did not change, and no phase segregation was observed. (data not shown).

A series of Ce_{0.15}Zr_{0.85}O₂ (CZ) supports and Pt supported on CZ catalysts were characterized by nitrogen physisorption (Table I). As listed in Table I, surface areas of ceria-zirconia solid solutions greatly increased (above 50 m²/g) compared to those of cerium oxide or zirconium oxide itself. The specific surface areas of fresh CZ samples are in the order of CZH < CZM < CZC < CZS, where CZS method exhibits much higher surface area than that of CZH. The isotherms of all samples are identified as type IV and hysteresis, characteristic of mesoporous material (data not shown).

Figures 2(a) and (b) show the H₂-TPR profiles of CeZrO₂ mixed oxides with different support composition and 2 wt% Pt/CZ catalysts, respectively. Cerium oxide is well known for its facile reducibility compared with other

Table I. Textural properties of ceria-zirconia supports and Pt containing catalysts.

Sample	S_{BET} (m ² g ⁻¹)	V_t (cm ³ g ⁻¹)	w_{BHH} (nm)
CeO ₂	3.9	0.869	34.21
ZrO ₂	3.4	0.014	27.64
CZC	90.6	0.198	6.11
CZS	107.3	0.322	9.05
CZH	51.6	0.253	15.84
CZM	73.2	0.123	6.10
Pt/CZC	78.2	0.252	9.70
Pt/CZS	91.3	0.259	8.19
Pt/CZH	46.1	0.222	15.33
Pt/CZM	61.5	0.104	5.13

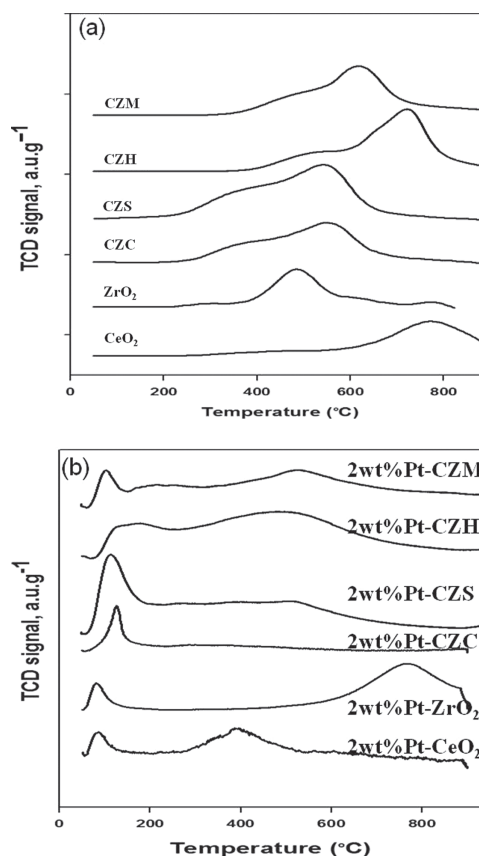


Fig. 2. H₂-TPR profiles of (a) CZs and (b) Pt/CZ catalysts.

fluorite-type oxide. CeO₂ itself exhibits two peaks: the small one at 550 °C and the big one with a maximum at around 800 °C as reported in literature.¹⁸ It is known that in Ce-Zr solid solution, the reduction of ceria occurs concurrently at the surface and the bulk. As shown in Figure 2(a), two distinct peaks appeared in all CZ samples and temperature of big consumption peaks were shifted from 780 °C of CeO₂ to lower temperatures in the range of 560 °C and 720 °C. A peak appears at 720 °C in the TPR profile of the CZH, which is ascribed to the reduction of the bulk oxygen and is usually observed over ceria.^{19,20} In case of CZM, temperature of bulk oxygen reduction peak moved to lower temperature of 620 °C. However, for the other samples (CZS and CZC), the reduction temperature of the bulk oxygen decreases greatly from 800 to 580 °C, indicating the increase of bulk oxygen mobility, thus improving the reducibility of bulk oxygen. Reducibility of CZ samples is following order: CZS, CZC > CZM > CZH. After the Pt incorporation, a single sharp main peak was observed at temperature between 100 and 200 °C for all Pt/CZ samples, which may be attributed to the reduction of platinum oxide and to the reduction of mixed oxide catalyzed by platinum.¹⁹ Usually, for ceria that is not doped with Zr, 1% Pt addition catalyzes the surface reduction step to around 225–300 °C. Moreover, the addition of Zr further shifts this peak to lower temperature, even

below 200 °C in the 25–75% Zr addition range. In this study, the consumption peaks of bulk oxygen reduction still maintained in TPR profiles of Pt/CZH, Pt/CZM and Pt/CZS. However, the amount of hydrogen consumed during the reduction of Pt/CZS catalyst in low temperature region (< 200 °C) was the largest, suggesting that Pt/CZS could prefer to reforming reaction.

The use of structure insensitive reactions to determine Pt dispersions on ceria containing samples is growing since most traditional techniques such as H₂ or CO chemisorption are not recommended for these catalysts due to the possibility of adsorption of both gases on ceria.¹⁵ Cyclohexane dehydrogenation rates and calculated platinum dispersions from these rates are listed in Table II. Pt/CZS, Pt/CZM and Pt/CZC showed very similar Pt dispersion values even though Pt dispersion of Pt/CZS was the highest. These values are improved by around 36% compared to those of Pt/CeO₂ or Pt/ZrO₂. However, Pt/CZH exhibited much lower Pt dispersion than other Pt/CZ catalysts, which could be attributed to its lowest surface area among Pt/CZ catalysts.

3.2. Effect of Support on the APR Activity

Aqueous phase reforming of 10 wt.% ethylene glycol over Pt/CZ catalysts was carried out to investigate an effect of supports on catalytic activities. Table II shows the rate of hydrogen production of 2 wt% Pt metal loaded on CZH, CZM, CZC, and CZS. The rate of hydrogen production was greatly affected by the kinds of support employed. The supported Pt catalysts can be ranked in the following order with respect to the volumetric hydrogen production rate: Pt/CZH < Pt/CZM ≤ Pt/CZC < Pt/CZS. In addition, the sol-gel based catalysts show relatively higher conversion of carbon to gas and higher hydrogen yield than those of other catalysts from different support. The highest APR activity of Pt/CZS catalyst might be due to the Pt dispersion and reduction degree of sol-gel based catalyst comparing with other catalysts as shown in Table II and Figure 2. However, Pt dispersion and reducibility of Pt/CZ catalysts did not show an absolute linear correlation to APR activity. Pt/CZS, Pt/CZM and Pt/CZC with similar Pt dispersion showed different activity and the reducibility of CZS and CZC supports are similar but the activity of the former is much higher than the latter. It is evident that

Table II. Effect of catalyst support on APR activities over the Pt/CZ catalyst (10 wt% EG, 250 °C, WHSV of 2.0 h⁻¹).

Catalysts	Conversion (%)	H ₂ rate (cc/g _{cat} · min)	H ₂ yield (%)	Apparent dispersion (%)	H ₂ TOF (h ⁻¹)
Pt/CeO ₂	10.5	6.7	10.0	24.8	39.0
Pt/ZrO ₂	10.4	10.7	16.0	22.0	70.3
Pt/CZC	20.2	16.1	22.1	33.1	70.2
Pt/CZS	29.4	20.0	30.1	33.8	86.2
Pt/CZH	14.2	10.0	15.1	23.7	61.4
Pt/CZM	19.6	15.8	21.7	33.7	68.0

higher Pt dispersion and reducibility of catalysts are more favorable for APR activity in view of Pt/CZS but porous structure such as surface area and pore size distribution of catalysts could be another important factor for determining APR activity.

Figure 3(a) shows the effect of temperature and pressure on APR activities over Pt/CZS catalyst with 2.0 h⁻¹ of WHSV. As increasing temperatures from 210 to 250 °C, system pressure should be adjusted enough to maintain a liquid phase. Thus, pressure and temperature strongly interact with each other due to changes in solubility of CO₂ and H₂. Generally, increase of temperature results in an increase in APR activity; such as the conversion of carbon to gas, H₂ yield, and H₂ selectivity as well as the decrease of alkane selectivity. Thus, increasing temperature and pressure can promote the C–C bond cleavage and WGS reaction.

Contact time of reactants over the catalyst has a significant impact on the reforming process. In this work, reforming results were compared at different liquid hourly space velocities (WHSV), 1.0 h⁻¹ to 6.0 h⁻¹. Figure 3(b) shows that the lower WHSV of 1.0 h⁻¹ produced a higher

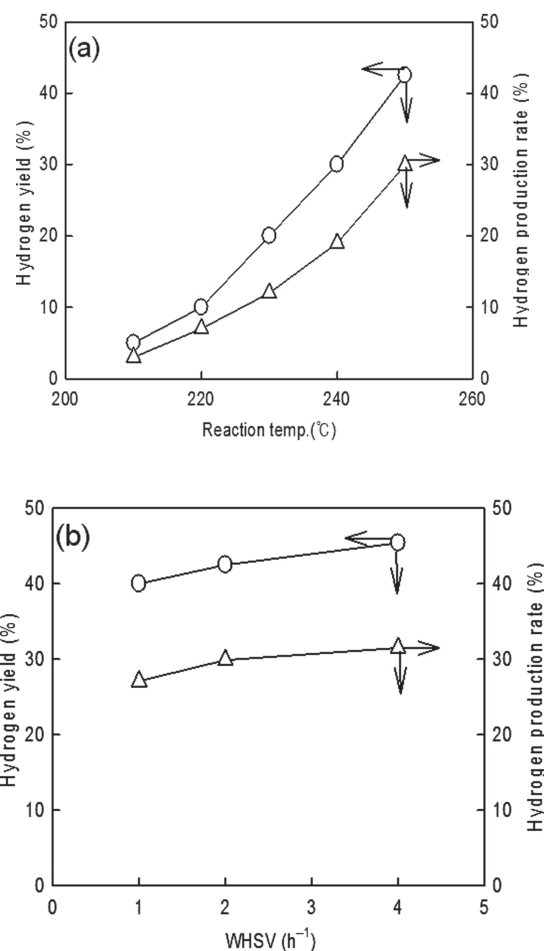


Fig. 3. Effect of (a) temperature and (b) weight hourly space velocity on APR activities over Pt/CZS catalyst.

hydrogen yield and the conversion of carbon to gas selectivity without decreasing the selectivity of hydrogen and alkane with WHSV. However, a higher hydrogen production rate was obtained at 6.0 h⁻¹. Investigation of the influence of WHSV demonstrated that lower WHSV (longer contact time) could facilitate conversion of ethylene glycol into hydrogen and the reforming ratio of hydrogen to carbon dioxide was also close to the theoretical value of 2.5, while at a higher WHSV, this can be attributed to a shorter contact time for the ethylene glycol reactant with the catalyst that allows the reforming reaction to take place, while shorter contact time only allows the partial conversion of ethylene glycol.

4. CONCLUSION

The effect of support on the aqueous phase reforming of ethylene glycol over 2 wt% Pt/Ce_{0.15}Zr_{0.85}O₂ catalysts has been investigated. It was found that the support effect on the activity of 2 wt% Pt/Ce_{0.15}Zr_{0.85}O₂ catalysts with different preparation method was given as follows: CZH < CZM ≤ CZC < CZS. It was suggested that the catalytic activity for reforming of ethylene glycol is dependent on degree of reduction, Pt dispersion and porous structure properties. 2 wt% Pt/Ce_{0.15}Zr_{0.85}O₂ (CZS) catalyst showed good catalytic activity for APR reaction due to its high metal dispersion and reducibility. On the effect of reaction conditions such as reaction temperature and WHSV, the hydrogen production rate and hydrogen yield increased in proportion to the reaction temperature and corresponding system pressure, whereas WHSV slightly affected APR activity.

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