Water–gas shift reaction over Pt and Pt–CeO$_x$ supported on Ce$_x$Zr$_{1-x}$O$_2$

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ABSTRACT

The water–gas shift (WGS) reaction was examined over Pt and Pt–CeO$_x$ catalysts supported on Ce$_x$Zr$_{1-x}$O$_2$ (Ce$_{0.05}$Zr$_{0.95}$O$_2$, Ce$_{0.2}$Zr$_{0.8}$O$_2$, Ce$_{0.4}$Zr$_{0.6}$O$_2$, Ce$_{0.6}$Zr$_{0.4}$O$_2$, Ce$_{0.7}$Zr$_{0.3}$O$_2$ and Ce$_{0.8}$Zr$_{0.2}$O$_2$) under severe reaction conditions, *viz.* 6.7 mol% CO, 6.7 mol% CO$_2$, and 33.2 mol % H$_2$O in H$_2$. The catalysts were characterized with several techniques, including X-ray diffraction (XRD), CO chemisorption, temperature-programmed reduction (TPR) with H$_2$, temperature-programmed oxidation (TPO), inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and bright-field transmission electron microscopy (TEM). Among the supported Pt catalysts tested, Pt/Ce$_{0.4}$Zr$_{0.6}$O$_2$ showed the highest WGS activity in all temperature ranges. An improvement in the WGS activity was observed when CeO$_x$ was added with Pt on Ce$_x$Zr$_{1-x}$O$_2$ supports (x = 0.05 and 0.2) due to intimate contact between Pt and CeO$_x$ species. Based on CO chemisorptions and TPR profiles, it has been found that the interaction between Pt species and surface ceria-zirconia species is beneficial to the WGS reaction. A gradual decrease in the catalytic activity with time-on-stream was found over Pt and Pt–CeO$_x$ catalysts supported on Ce$_x$Zr$_{1-x}$O$_2$, which can be explained by a decrease in the Pt dispersion. The participation of surface carbonate species on deactivation appeared to be minor because no improvement in the catalytic activity was found after the regeneration step where the aged catalyst was calcined in 10 mol% O$_2$ in He at 773 K and subsequently reduced in H$_2$ at 673 K.

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1. Introduction

Fuel cells, which are regarded as highly efficient energy-conversion systems, have attracted considerable attention, and therefore, the concomitant development of a fuel processor in which hydrocarbon fuels are converted into hydrogen (H$_2$) is also in demand [1]. The water–gas shift (WGS) reaction (CO(g) + H$_2$O(g) ↔ CO$_2$(g) + H$_2$(g) = −41,166 J/mol) is one of the key steps in a fuel processing system, which can increase H$_2$ concentration as well as decrease CO concentration. Although Cu-based catalysts have been used in the commercial WGS process carried out at low temperatures, their applications in electric vehicles or residential power-generators have been considered to be limited because of the low thermal stability and pyrophoric property of these catalysts [2]. Fuel cell companies are currently using Cu-based WGS catalysts by controlling shutdown and start up conditions to avoid the environments that create these problems.

Nevertheless, precious metal catalysts have been examined as substitutes for Cu-based catalysts: Pt catalysts have been reported to show higher WGS activity over a wide temperature range than others based on Rh, Ru, Pd, and Ir [3].

To increase the catalytic activity for supported Pt catalysts, various supports including CeO_2 [4–18], ZrO_2 [11–19], and $Ce_xZr_{1-x}O_2$ [3–5,15–21], have been examined. It has also been reported that the WGS activity of Pt could be enhanced by the addition of a second metal, such as an alkali metal (Li, Na, K, Rb, and Cs) [10,19,22], an alkali earth metal (Ba, Mg, Sr, and Ca) [4,23], a rare earth element (Y, La, Ce, Nd, Sm, Eu, Gd, Ho, Er, Tm, and Yb) [4,5,11,13,14,19], or a transition metal (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, and Re) [4,11,17,19]. Among them, Pt/$Ce_xZr_{1-x}O_2$ catalysts have been reported to be active. Flytzani-Stephanopoulos et al. proposed that the presence of the Ce ions could stabilize the oxidized active site Pt species irrespective of the support medium [9,22]. It was also suggested that the introduction of Zr^{4+} into ceria to form a binary mixed phase lead to the increase in the oxygen mobility of ceria as well as the increase in its reducibility, resulting in the enhanced WGS activity [5,15]. Recently, it was proposed that the intimate contact between Pt and ceria on a support was a crucial factor in the WGS reaction [13,14,19]. Therefore, studying the effect of additional ceria on the WGS activity for Pt/$Ce_xZr_{1-x}O_2$ is necessary. In this study, we compared the WGS activity over Pt and Pt–CeO_x catalysts supported on $Ce_xZr_{1-x}O_2$ and tried to explain the differences in catalytic activity with various characterization methods.

2. Experimental

2.1. Catalyst preparation

Various supports, viz. $Ce_{0.05}Zr_{0.95}O_2$, $Ce_{0.2}Zr_{0.8}O_2$, $Ce_{0.4}Zr_{0.6}O_2$, $Ce_{0.6}Zr_{0.4}O_2$, $Ce_{0.7}Zr_{0.3}O_2$, and $Ce_{0.8}Zr_{0.2}O_2$, were prepared from $Ce(NO_3)_3 \cdot 6H_2O$ (Junsei Chemical Co.) and $ZrCl_2O \cdot 8H_2O$ (Junsei Chemical Co.) by the co-precipitation method. An aqueous solution of ammonia, used as a precipitation agent, was added dropwise until the pH of the aqueous solution containing the cerium and zirconium precursors was adjusted to ca. 9–10. The resulting slurry was aged for 2 h at 333 K with constant

stirring. After the precipitate was washed and filtered using DI water, it was dried at 393 K overnight and calcined in air at 773 K.

Supported Pt catalysts were prepared by the wet impregnation method from a support and an aqueous solution of $Pt(NH_3)_4(NO_3)_2$ (Aldrich). Supported CeO_x-promoted Pt catalysts were prepared by the co-impregnation method from a support and an aqueous solution of $Pt(NH_3)_4(NO_3)_2$ (Aldrich) and $Ce(NO_3)_3 \cdot 6H_2O$ (Junsei Chemical Co.). The content of Pt was intended to be 1 wt%. The amount of Ce added as a promoter was intended to be fixed at 3.6 wt% for Pt–CeO_x/$Ce_xZr_{1-x}O_2$. All of the catalysts were calcined in air at 773 K and reduced in a hydrogen stream at 673 K for 1 h before the reaction. To differentiate each catalyst, the molar ratio of Ce/(Ce + Zr) in a support used for each catalyst is denoted as x in $Ce_xZr_{1-x}O_2$ (x = 0.05, 0.2, 0.4, 0.6, 0.7, and 0.8).

2.2. Catalyst characterization

The chemical composition of the prepared samples was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, JY-70Plus, Jobin-Yvon); the results are listed in Table 1.

The BET surface area was calculated based on the N_2 adsorption data obtained using a Gemini apparatus (Micromeritics) at liquid N_2 temperature. Before the measurement, the sample was degassed under vacuum for 4 h at 473 K. The BET surface area for each catalyst is shown in Table 1.

The bulk crystalline structures of the catalysts were determined by the X-ray diffraction (XRD) technique. The XRD patterns were obtained with a Rigaku D/MAC-III using Cu Kα radiation (λ = 0.15406 nm), operated at 50 kV and 30 mA (1.5 kW). The assignment of the crystalline phases was carried out using PCPDFWIN software (version 2.2) with the ICDD database.

CO chemisorptions were carried in an AutoChem 2910 unit (Micromeritics) equipped with a thermal conductivity detector (TCD) to measure the CO uptake and an on-line mass spectrometer (QMS 200, Pfeiffer Vacuum) to detect any organic or inorganic species in the effluent stream during CO chemisorption. Quartz U-tube reactors were generally loaded with 0.10 g of the sample. The catalysts were pretreated by

Catalysts	BET surface area (m²/g)	Bulk composition (wt.%)[a]			Ce/(Ce + Zr) molar ratio
		Pt	Ce	Zr	
Pt/$Ce_{0.2}Zr_{0.8}O_2$	73	0.9	22.3	49.6	0.23
Pt/$Ce_{0.4}Zr_{0.6}O_2$	76	0.6	39.4	33.7	0.43
Pt/$Ce_{0.6}Zr_{0.4}O_2$	77	0.7	49.3	22.6	0.59
Pt/$Ce_{0.8}Zr_{0.2}O_2$	75	0.8	63.7	10.5	0.80
Pt–CeO_x/$Ce_{0.05}Zr_{0.95}O_2$	72	0.8	7.5	72.2	0.06
Pt–CeO_x/$Ce_{0.2}Zr_{0.8}O_2$	76	0.6	19.1	50.8	0.20
Pt–CeO_x/$Ce_{0.4}Zr_{0.6}O_2$	69	0.8	40.3	31.4	0.46
Pt–CeO_x/$Ce_{0.6}Zr_{0.4}O_2$	80	0.7	50.4	22.6	0.59
Pt–CeO_x/$Ce_{0.7}Zr_{0.3}O_2$	69	0.8	59.3	15.4	0.71
Pt–CeO_x/$Ce_{0.8}Zr_{0.2}O_2$	77	0.7	62.2	10.2	0.80

Table 1 – Physical properties of the supported Pt and Pt–CeO_x catalysts.

a The bulk composition was analyzed by ICP-AES.