Water-gas Shift Reaction over Ceria-promoted Pt catalysts

Yong Tae Kim[1], Eun Duck Park[1*], Hyun Chul Lee[2], Doohwan Lee[2] and Kang Hee Lee[2]
[1]*Division of Energy Systems Research, Ajou University, Suwon, 443-749 (Korea)*
[2]*Samsung Advanced Institute of Technology (SAIT), Yongin, 446-712 (Korea)*
*edpark@ajou.ac.kr

Introduction

The fuel processor in which hydrocarbon fuels can be converted into hydrogen has recently attracted much attention as a result of the advancement in the fuel cell technology. In a fuel processor, the water-gas shift (WGS) reaction plays a crucial role in the transformation of CO, a well-known poisonous gas to electrode of fuel cell, into hydrogen through reaction with steam. In WGS reaction, conventional commercial Cu-based catalysts suffer from some drawbacks to be applied to a small-scale fuel processor with characteristics such as a cyclic operation and possibility for air contamination [1]. To overcome these weak points of commercial WGS catalysts, some noble metal catalysts including Au and Pt group metals have been extensively studied [2]. Although intensive works have been conducted to find out the WGS catalysts both active at low temperatures and stable during various operation modes, there is still need to develop the advanced WGS catalyst to be applied for practical application [3]. In this work, we have found that Pt-Ce/TiO_2 prepared by a single-step co-impregnation method shows the highest WGS activity at low temperatures among ceria-promoted Pt catalysts supported on γ-Al_2O_3, SiO_2, TiO_2 (P-25), CeO_2, SiO_2-Al_2O_3, yttria-stabilized zirconia (YSZ) and ZrO_2. Furthermore, the nice correlation can be made between the low-temperature water-gas shift activity and the amounts of chemisorbed CO as well as the reducibility of ceria near Pt at low temperatures.

Materials and Methods

All the catalysts were prepared with a wet impregnation method. All the Pt-Ce/support catalysts were prepared with a co-impregnation method. Pt/Ce/TiO_2 and Ce/Pt/TiO_2 were prepared by a sequential impregnation. All the catalysts were calcined at 773 K in air and reduced at 673 K in a hydrogen stream for 1 h before a reaction. For catalytic tests, a standard gas of 6.7 vol. % CO, 6.7 vol. % CO_2 and 33.2 vol. % H_2O balanced with H_2 was fed to the reactor at an atmospheric pressure. For the stability test in the cyclic operation, a standard gas of 6.3 vol% CO, 6.3 vol% CO_2, and 37.5 vol% H_2O in balanced H_2 was fed to the reactor, in which 2.5 g of catalyst without diluents was contacted with a reactant gas at a flow rate of 250 ml/min, at an atmospheric pressure. The catalytic activity was measured with a ramping rate of 1 K/min from 423 to 623 K. The N_2 physisorption, the temperature-programmed reduction with H_2 (H_2-TPR) and CO chemisorption were conducted to characterize catalysts.

Results and Discussion

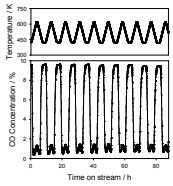
Based on the comparison work for WGS reaction over ceria-promoted Pt catalysts supported on various supports such as γ-Al_2O_3, SiO_2, TiO_2 (P-25), CeO_2, SiO_2-Al_2O_3, yttria-stabilized zirconia (YSZ) and ZrO_2, Pt-Ce/TiO_2 can be selected to show the highest WGS activity. The effect of preparation sequence of Pt and ceria in ceria-promoted Pt/TiO_2 on the WGS activity was examined as shown in Table 1. Pt-Ce/TiO_2 prepared with a single-step co-impregnation method showed the highest WGS activity among ceria-promoted Pt/TiO_2. Based on H_2-TPR, the WGS activity appeared to increase with decreasing the peak position of the low temperature reduction (LTR) peak and increasing the peak intensity at LTR region. Most of ceria on the surface were determined to be reduced at low temperature in the active catalysts. The reaction rate over ceria-promoted Pt catalysts supported on TiO_2 generally increased with increasing the amount of CO chemisorption. This catalyst also showed the stable WGS activity during 10 cyclic operations as displayed in Fig. 1.

Table 1. The physicochemical data of Pt/TiO_2 and ceria-promoted Pt/TiO_2 catalysts and their catalytic activities for water gas shift reaction.

Catalysts (Ce/Pt=5)	CO chem. (μmol/$g_{cat.}$)	H_2-TPR		Reaction rate at 543K (μmol/g_{cat}·s)	Normalized reaction rate at 543K[a] (s^{-1})
		Peak position (K)	μmol H_2 / $g_{cat.}$		
Pt/ TiO_2	8.6	366.0	19.0	5.0	0.58
Ce/Pt/ TiO_2	20.4	414.2	58.3	10.9	0.53
Pt/ Ce/ TiO_2	16.8	410.5	63.2	5.6	0.33
Pt-Ce/ TiO_2	50.0	355.7	143.0	16.4	0.32

[a]The normalized reaction rate is calculated by dividing the reaction rate with the amount of chemisorbed CO

Figure 1. The thermal cyclic test of Pt-Ce/TiO_2 (Ce/Pt=5) for WGS reaction. The feed composition: 6.3 vol.% CO, 6.3 vol.% CO_2, 37.5 vol.% H_2O in H_2. F/W= 100 ml/min/$g_{cat.}$



Significance

The close correlation between the low-temperature water-gas shift activity and the amounts of chemisorbed CO as well as the reducibility of ceria near Pt at low temperatures has been observed over Pt-Ce/TiO_2 which was determined to be most active among ceria-promoted Pt catalysts supported on γ-Al_2O_3, SiO_2, TiO_2 (P-25), CeO_2, SiO_2-Al_2O_3, yttria-stabilized zirconia (YSZ) and ZrO_2.

References

1. O. Ilinich, W. Ruettinger, X.S. Liu, R. Ferrauto, *J. Catal.* 247, 112 (2007).
2. D.L. Trimm, *Appl. Catal. A: Gen.* 296, 1 (2005).
3. W. Ruettinger, X. Liu, R.J. Farrauto, *Appl. Catal. B: Environ.* 65, 135 (2006).