Contents lists available at SciVerse ScienceDirect







journal homepage: www.elsevier.com/locate/apcata

A study on the effect of support's reducibility on the reverse water-gas shift reaction over Pt catalysts

Sung Su Kim, Hyun Hee Lee, Sung Chang Hong*

Department of Environmental Energy Systems Engineering, Kyonggi University, 94 San, lui-dong, Youngtong-ku, Suwon-si, Gyeonggi-do, 442-760, Republic of Korea

ARTICLE INFO

ABSTRACT

Article history: Received 14 October 2011 Received in revised form 1 February 2012 Accepted 16 February 2012 Available online 24 February 2012

Keywords: Pt TiO₂ RWGS Catalyst In this study, the effect of the reducibility of the support on the mechanism of the reverse water gas shift reaction over Pt/TiO₂ and Pt/Al₂O₃ catalysts was examined using a differential and fixed bed reactor. The kinetic study showed that the reverse water gas shift reaction using the Pt/TiO₂ and Pt/Al₂O₃ catalysts were consistent with the redox mechanism. An elementary reaction test and XPS analysis further confirmed that the reverse water gas shift reaction proceeded through the redox mechanism via oxidation and reduction at the Pt sites and reducible support sites on the catalyst surface. In the H₂ TPR and FT-IR experiments, the Pt/TiO₂ catalyst produced greater CO₂ conversion and TOFs due to the presence of the new active site, which resulted from the strong metal–support interaction and higher reducibility of the support relative to the Pt/Al₂O₃ catalyst.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Environmental problems due to the emission of pollutants through the combustion of solid, liquid and gaseous fuels in various stationary and mobile energy systems as well as emissions from manufacturing plants have become a major global problem involving not only pollutants such as NOx, SOx, and particulate matter, but also greenhouse gases (GHG) such as carbon dioxide (CO₂) and methane (CH₄). In particular, global climate change has been gradually accelerating and is now considered a global issue of imperative importance.

The most direct solution to resolve global climate change is to reduce CO_2 , which is primarily achieved through chemical conversion of CO_2 . The conversion of CO_2 to chemical resources has been accomplished using several methods [1–3]. The catalytic hydrogenation of CO_2 to form methanol is one of the most efficient processes to treat large quantities of CO_2 , while minimizing hydrogen loss when compared with hydrocarbon production [4]. Park et al. [4] and Joo et al. [5] developed the CAMERE (carbon dioxide hydrogenation to form methanol via a reverse-water-gas-shift reaction) process to convert CO_2 into methanol. The key reaction of this process was the reverse-water-gas-shift reaction (RWGS reaction) [6]. The RWGS is a moderately endothermic reaction and can be described by the following equation.

Reverse Water Gas Shift Reaction

 $\text{CO}_2 + \text{H}_2 \rightarrow \text{ CO} \ + \ \text{H}_2 \text{O}, \quad \Delta H_{298\,\text{K}} = \ 41.19\,\text{kJ/mol}$

Most catalysts showing excellent reaction activity in the RWGS also display great activity in the WGS. Cu, Zn, Fe and Zn catalysts have been shown to display superior catalytic activity in these reactions [4,7,8]. Many studies have examined the use of the Pt catalyst in WGS (Water Gas Shift reaction) [9–12]. It has been reported that reactions using Pt/TiO₂, Pt/CeO₂ and Pt/CeO₂-TiO₂ catalysts, which have been shown to display strong metal support interactions, showed the best performance. However, very little work has been done to examine the activity of the Pt catalysts in the RWGS reaction.

Two main reaction mechanisms of the WGS reaction have been proposed. The first reaction mechanism is the 'redox' reaction. In this mechanism, CO(g) adsorbs on reduced metal sites to form a Me-CO. The Me-CO then reacts with an oxygen atom coming from the catalyst surface. The oxygen on the catalyst surface comes from two sources depending on the support. For reducible supports (TiO₂, CeO₂), the oxygen originates from the support itself. In contrast, for irreducible supports (Al₂O₃, SiO₂), the oxygen comes from the active metal. The reduced catalyst surface is subsequently reoxidized by H₂O, and H₂ is produced. The second mechanism is 'associative'. This mechanism is associated with the adsorption of CO, CO₂, H₂ and H₂O on the catalyst surface and the formation of formate caused by the surface reaction is the rate determining step.

Recently, Goguet et al. [13] examined the reaction mechanism and intermediates in RWGS over a Pt/CeO_2 catalyst. They insisted that the RWGS reaction proceeded via surface carbonate

^{*} Corresponding author. Tel.: +82 31 249 9733; fax: +82 31 254 4905. *E-mail address*: schong@kyonggi.ac.kr (S.C. Hong).

⁰⁹²⁶⁻⁸⁶⁰X/\$ - see front matter © 2012 Elsevier B.V. All rights reserved. doi:10.1016/j.apcata.2012.02.021