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Applied Catalysis A: General 298 (2006) 152–160

APPLIED CATALYSIS A: GENERAL

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Characterization of a Pt/TiO_2 (rutile) catalyst for water gas shift reaction at low-temperature

Hajime Iida *, Akira Igarashi

Department of Environmental Chemical Engineering, Faculty of Engineering, Kogakuin University,
2665-1 Nakano-machi, Hachioji-shi, Tokyo 192-0015, Japan

Received 2 May 2005; received in revised form 12 September 2005; accepted 27 September 2005

Abstract

Recently, we have reported that the Pt/TiO_2 (R: rutile) catalyst has relatively high activity for the water gas shift reaction at low-temperature (LT-WGS). In this study, Pt catalysts supported on TiO_2 (R), TiO_2 (A: anatase), ZrO_2 and Al_2O_3, were characterized by TEM, XPS, TPD, and FT-IR measurements. These results suggested detailed reasons for the high catalytic activity of the Pt/TiO_2 (R) catalyst. TEM micrographs showed that the Pt dispersion of the Pt/TiO_2 (R) catalyst was lower than those of the Pt/ZrO_2 and Pt/Al_2O_3 catalysts, although Pt/TiO_2 (R) had superior catalytic activity. Furthermore, the Pt/TiO_2 (R) catalyst had larger Pt dispersion than Pt/TiO_2 (A), although Pt/TiO_2 (R) had lower BET surface area than Pt/TiO_2 (A). XPS spectra indicated that the TiO_2 (R and A) supports had a stronger electronic effect with Pt than ZrO_2 and Al_2O_3. In addition, CO-TPD profiles revealed that the strength of Pt–CO bonding on Pt/TiO_2 (R) and Pt/TiO_2 (A) catalysts was weakened due to the interaction between the support and Pt. These results indicated that the catalytic activity of Pt catalysts for LT-WGS is greatly affected by the interaction between the support and Pt, rather than by Pt dispersion, although the difference in catalytic activity between the Pt/TiO_2 (R) and Pt/TiO_2 (A) catalysts can mainly be explained by the degree of Pt dispersion.

Finally, IR spectra of CO–H_2O and –D_2O reactions on the Pt catalysts indicated that the high catalytic activity of Pt/TiO_2 (R) could be attributed to the fast formation and decomposition of formate as a reaction intermediate.

Keywords: Water gas shift; Pt/TiO_2 (rutile); Surface hydroxyls; Adsorbed CO species; Bidentate formate

1. Introduction

The polymer electrolyte fuel cell (PEFC) system has attracted attention as a small-scale power source for residential use, vehicles, and portable electric devices. One of the main methods of hydrogen production for the PEFC system is the steam reforming (SR) of hydrocarbons such as natural gas and LPG. Catalytic reactors for the SR process are required to be extremely small for use in PEFC systems, unlike the catalytic reactor in a conventional large chemical plant. In the SR process, the water gas shift reaction at low-temperature (LT-WGS) is used to remove CO from the reformed gas. A Cu–Zn catalyst is conventionally used for LT-WGS, but this catalyst has low durability under an oxidizing atmosphere in the presence of steam. For example, daily start-up and shut down (DSS) operation is required in residential PEFC systems, requiring the venting of combustible gases for safety reasons. This purge treatment is performed under a stream of air or in a humid atmosphere, and not with a gas cylinder of inert gas such as N_2 in order to avoid enlargement of the system. Thus, the Cu–Zn catalyst for LT-WGS is deactivated under DSS operation.

There is therefore a need for a new LT-WGS catalyst to replace the commercial Cu–Zn catalyst. We have examined various precious metal catalysts in order to meet this demand, and have recently reported that Pt/TiO_2 (R: rutile) has a relatively higher catalytic activity than Pt/TiO_2 (A: anatase) for LT-WGS [1].

LT-WGS catalysts have often been characterized by TEM, XPS, TPD, and FT-IR measurements. Shido and Iwasawa have proposed a surface formate mechanism for LT-WGS on CeO_2, following FT-IR and TPD studies, and have suggested that formate decomposition is the rate-determining step [2,3]. Jacobs et al. have also proposed a formate mechanism for LT-WGS on Pt/CeO_2 and Pt/ThO_2 [4–6]. On the other hand, Gorte

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* Corresponding author.
E-mail address: iida@cc.kogakuin.ac.jp (H. Iida).

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doi:10.1016/j.apcata.2005.09.032

and co-workers have proposed a ceria-mediated redox process for LT-WGS on CeO_2 [7]. Furthermore, Boccuzzi et al. have proposed the reaction mechanism for LT-WGS over Au/Fe_2O_3, naming the essential aspects of the mechanism as the dissociative adsorption of water over ultrafine gold particles followed by a spillover of active OH groups onto adjacent sites on the ferric oxide with a redox reaction between Fe^{3+} and Fe^{2+} [8,9]. Thus, many researchers have characterized the LT-WGS catalysts, and have proposed various reaction mechanisms for LT-WGS. However, there has been no comparative study to probe the activity of Pt/TiO_2 (R) and Pt/TiO_2 (A) catalysts for LT-WGS.

The purpose of this study was to examine details of the superior catalytic activity of Pt/TiO_2 (R) compared to Pt/TiO_2 (A), Pt/ZrO_2, and Pt/Al_2O_3, using TEM, XPS, TPD and FT-IR measurements.

2. Experimental

2.1. Catalyst preparation

All Pt catalysts were prepared by a conventional impregnation method, as follows. The TiO_2 (R), TiO_2 (A), Al_2O_3, and ZrO_2 supports were obtained by calcining JRC-TIO-1, 3, JRC-ALO-6 (reference catalyst of the Catalysis Society of Japan), and a commercial zirconium hydroxide (Mitsuwa Chemical) in a stream of air at 500 °C for 1 h. An aqueous solution of platinum chloride hexa-hydrate was then added to the support powder. The mixture was evaporated on a water bath at 100 °C; the resultant material was dried at 100 °C for 15 h, and then finally calcined in a stream of air at 500 °C for 1 h. All Pt catalysts were prepared with Pt loadings of 3 wt.%.

2.2. Activity test

LT-WGS was performed using a conventional fixed bed flow reactor. The catalyst (0.5 ml) was placed in a reaction tube made of Pyrex glass, and was then reduced in an H_2 stream at 500 °C for 1 h. After the catalyst was cooled down at 175 °C in a N_2 stream, H_2O was supplied to the reactor using a micro feeder. Following the supply of steam, CO gas (purity 99.95%) was introduced into the reactor. Condensed water was extracted into an ice water trap located downstream of the reactor, and the gas composition was analyzed using a gas chromatograph with a thermal conductivity detector (TCD). The catalytic performance was measured every 25 °C from 175 to 275°C. The space velocity (on the basis of CO) was 9,500 h^{-1}, and the mole ratio of H_2O to CO was 1.5.

2.3. Characterization

2.3.1. BET surface area

The BET surface area of the newly prepared catalysts was determined by N_2 adsorption at 77 K using a flow absorption apparatus (Flow sorb II 2300, Micromeritics). The composition of the flow gas was N_2:He = 30:70. The catalyst was degassed at 200 °C for 15 min, prior to measurement.

2.3.2. TEM

The microstructure of the Pt catalysts was observed after LT-WGS, using transmission electron microscopy (TEM) with a JEM-2010F microscope (JEOL), at an acceleration voltage of 200 kV. Elemental analysis of the catalyst was performed using an energy-dispersive X-ray spectrometer (EDS: Noran) attached to the JEM-2010F.

2.3.3. XPS

X-ray photoelectron spectroscopy (XPS) measurements were performed using a quantum 2000 (Ulvac Phi) instrument with an X-ray Al anode. The beam diameter was 100 μm, and the acceleration voltage was 15 kV.

2.3.4. CO chemisorption

The amounts of chemisorbed CO on the reduced catalysts at 500 °C, and on the catalysts after LT-WGS, were estimated using a volumetric absorption apparatus (ASAP2010, Micromeritics) with a chemisorption unit. After the catalyst underwent a degassing treatment (200 °C, 8 h, under vacuum) and heat treatment (in the case of the reduced catalyst at 500 °C: 400 °C, 0.5 h, in an H_2 stream; in the case of the catalyst after LT-WGS: 300 °C, 0.5 h, in an He stream), the CO adsorption isotherm on the catalysts was obtained at 35 °C. The CO chemisorption on Pt was based on an assumed stoichiometry of Pt:CO = 1:1.

2.3.5. Pt dispersion

Pt dispersion (D_{co}) of the catalysts was calculated from the amount of chemisorbed CO. D_{co} was defined as follows:

$$D_{co} = \frac{\frac{V_{co}}{0.0224} \times f_{CO/Pt}}{\frac{L_{Pt}}{M_{Pt}}} \tag{1}$$

where V_{CO} (m^3_{-STP}/g_{-cat}) is the amount of chemisorbed CO on the catalyst, L_{co} (−), the Pt content in the catalyst, $f_{CO/Pt}$ (−) (=1.0), the stoichiometric factor for CO chemisorption on Pt, and M_{Pt} (g/mol) is the atomic weight of Pt.

Pt dispersion (D_{TEM}) of the catalysts was also estimated from the dimensions of Pt particles in the TEM micrographs. D_{TEM} was defined as follows:

$$D_{TEM} = 6 \times \frac{\frac{M_{Pt}}{N \times \rho_{Pt}}}{\delta} \times \frac{1}{d_{Pt}} \tag{2}$$

where N (−) is Avogadro's constant, ρ (g/m^3) is the density of Pt, δ (m^2) is the cross-sectional area of a Pt atom, and d_{Pt} (m) is the mean diameter of Pt particles estimated from the TEM micrographs.

2.3.6. Turn over frequency (TOF)

The turn over frequency (TOF) of LT-WGS was defined as follows:

$$\mathrm{TOF} = \frac{F_{co} \times X_{co}}{V_{co}/0.0224 \times W_{cat}} \tag{3}$$

where F_{CO} (mol s^{-1}) is the CO molar flow rate, X_{CO} (−), the CO conversion at 250 °C, and W_{cat} (g) is the catalyst weight.