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Structure characterization of Pt-Re/TiO_2 (rutile) and Pt-Re/ZrO_2 catalysts for water gas shift reaction at low-temperature

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Abstract

Pt-Re/TiO_2 (R: rutile) and Pt-Re/ZrO_2 catalysts, which have superior catalytic activity for the water gas shift reaction at low temperature (LT-WGS), were characterized by TEM and XPS measurements in order to examine the role of Re in enhancing catalytic activity. For the TiO_2 (R)-supported catalysts, TEM micrographs showed that Pt dispersion increased by Re addition to Pt/TiO_2 (R). XPS spectra indicated that the electronic interaction between Pt and Re on the TiO_2-supported catalysts is stronger than that on the ZrO_2-supported catalysts, and that the state of Re was stable on Pt-Re/TiO_2 (R) under the LT-WGS conditions. These results indicate that one of reasons for the superior catalytic activity of Pt-Re/TiO_2 (R) catalyst is an increase in Pt dispersion. The stable Re acts as anchors for Pt particles, resulting in high Pt dispersion. On the other hand, for the ZrO_2-supported catalysts, TEM micrographs showed that the Pt dispersion decreased by Re addition to Pt/ZrO_2. XPS spectra indicated that the interaction between Re and support on Pt-Re/ZrO_2 catalysts is stronger than that on Pt-Re/TiO_2 (R), and that the redox reaction between Re^{4+} and Re^{7+} was repeated on Pt-Re/ZrO_2 in the course of the LT-WGS reaction. These results suggested that the Re redox reaction significantly contributes to the high catalytic activity of the Pt-Re/ZrO_2 catalyst, although Pt-Re/ZrO_2 had lower Pt dispersion than Pt/ZrO_2. Therefore, it was determined that the additive effect of Re on Pt dispersion and catalytic activity was largely affected by the state of Re.

Keywords: Water gas shift reaction at low-temperature (LT-WGS); Pt-Re/TiO_2 (R: rutile); Pt-Re/ZrO_2; Pt dispersion; Re redox reaction

1. Introduction

In the hydrogen production process by steam reforming of hydrocarbons for a polymer electrolyte fuel cell (PEFC) system, the reformed gas contains CO, which deteriorates a Pt electrode of PEFC, from several percent to approximately 10% as a equilibrium composition. The gas reformed from hydrocarbons has higher CO concentration than that from methanol, so that the CO concentration must be reduced below 1% by the water gas shift reaction at low temperature (LT-WGS), prior to preferential CO oxidation (PROX). Although a Cu-Zn catalyst is conventionally used for the LT-WGS, this catalyst deactivates by daily start-up and shut down (DSS) operation under the oxidizing atmosphere. Therefore, precious metal catalysts such as Au [1–3] and Pd [4], with superior durability are often used for LT-WGS; the catalysts supported on CeO_2 [1,4], and TiO_2 [2], and Fe_2O_3 [3] have been known to be effective for LT-WGS.

The authors have previously found that Pt/TiO_2 and Pt/ZrO_2 catalysts have relatively high catalytic activity for the LT-WGS. Further, it has been found that Re addition to Pt/TiO_2 and Pt/ZrO_2 causes an increase in catalytic activity. In particular, the Pt-Re/TiO_2 (R: rutile) catalyst has a higher catalytic activity compared to a commercial Cu-Zn catalyst [5]. However, detailed reasons for the higher catalytic activity resulting from Re addition to Pt/TiO_2 (R) and Pt/ZrO_2 catalysts have not yet been determined. Choung et al. have reported that the addition of Re to Pt/CeO_2-ZrO_2 catalysts enhances activity for the LT-WGS [6]; however, the role of Re in enhancing the catalytic activity is not well understood.

Pt-Re catalysts reported in a 1968 Patent [7] have been widely used in the naphtha reforming process. In order to clarify the additive effect of Re, many researchers have characterized the Pt-Re catalysts. However, there are a variety of morphologies of Pt and Re particles and several views on

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the role of Re on the Pt-Re catalysts [8–10], and these have not yet been clarified, because it is difficult to characterize the nature of highly dispersed Pt and Re on the catalysts. Furthermore, Pt-Re catalysts are sensitive to the conditions of catalyst preparation, such as the types of metal precursors and/or support used, the Pt or Re loadings, the calcination temperature, the reduction temperature, and so on [11,12]. The aim of this study was to examine details of the increase in catalytic activity that resulted from the Re addition to Pt/TiO_2 (R) and Pt/ZrO_2 using TEM and XPS measurements.

2. Experimental

2.1. Catalyst preparation

All catalysts were prepared by a conventional impregnation method, as follows. The TiO_2 (R) and ZrO_2 supports were obtained by calcining JRC-TIO-3 (reference catalyst of the Catalysis Society of Japan) and a commercial zirconium hydroxide (Mitsuwa Chemicals) in a stream of air at 500 °C for 1 h. Precursors used for Pt and Re were platinum chloride hexa-hydrate and ammonium perrhenate, respectively. The detailed procedure has been previously described [13]. For the Pt-Re catalysts, the impregnation of Re on TiO_2 (R) or ZrO_2 was carried out prior to the impregnation of Pt ("Pt-Re/TiO_2 (R)" or "Pt-Re/ZrO_2"). All catalysts were prepared with Pt and Re loadings of 3 wt% and 2 wt%, respectively.

In order to examine the effect of impregnation sequences of Pt and Re on catalytic activities, the Pt-Re co-impregnated catalysts ("PtRe/TiO_2 (R)", "PtRe/ZrO_2") and the Re impregnated on Pt catalysts ("Re-Pt/TiO_2 (R)" and "Re-Pt/ZrO_2") were also prepared.

2.2. Activity test

LT-WGS was performed using a conventional fixed bed flow reactor. The catalyst (0.25 ml) was diluted to 0.5 ml with quartz sand, placed in a reaction tube made of Pyrex glass and then reduced in a H_2 stream at 500 °C for 1 h. The feed gas was a quasi-reformed gas (CO 10%, CO_2 15%, H_2 75%). The total space velocity was 40,000 h^{-1}, and the mole ratio of H_2O to CO was 5.0. The details of this procedure have been previously described [13].

2.3. Characterization

The microstructure of the catalysts after LT-WGS was observed using transmission electron microscopy (TEM). The turn over frequencies (TOF) of the LT-WGS were calculated from the Pt particle size measured using TEM micrographs. In addition, the electronic states of Pt and Re were examined using X-ray photoelectron spectroscopy (XPS) measurements. The details of characterization have been previously described [13].

3. Results and discussion

3.1. Effect of impregnation sequence of Pt and Re

Fig. 1 shows the effect of the impregnation sequence of Pt and Re on the catalytic activities. This result indicates that the addition of Re to Pt/TiO_2 (R) and Pt/ZrO_2 induced the increase in catalytic activities, unrelated to the impregnation sequence. The effect of impregnation sequence is smaller than that of Re addition.

Therefore, the decisive reason of the increase in catalytic activity due to Re addition is little related to the impregnation sequence. In this study, the "Pt-Re" catalysts, which were prepared by impregnating Pt on Re catalysts, were characterized.

3.2. Structure of Pt and Re particles

Fig. 2 shows the TEM micrographs for Pt/TiO_2 (R), Pt-Re/TiO_2 (R), and Re/TiO_2 (R) catalysts after the LT-WGS reaction. Nano-particles were observed on Pt/TiO_2 (R) (Fig. 2(a)). Generally, for Re/TiO_2 (R), there were few nano-particles (Fig. 2(c)), although fine particles with a size of 1 nm or less were observed locally (Fig. 2(c, inset). Okal et al. have concluded that Re exists as very small clusters (<1 nm) that are undetectable using TEM measurements of a 1.05 wt% Re/γ-Al_2O_3 catalyst reduced at 550 °C [14]. It therefore appears that Re was present as highly dispersed clusters (<1 nm) or metal oxide nano-particles on Re/TiO_2 (R) with too low contrast sensitivity in the TEM micrograph. For Pt-Re/TiO_2 (R)

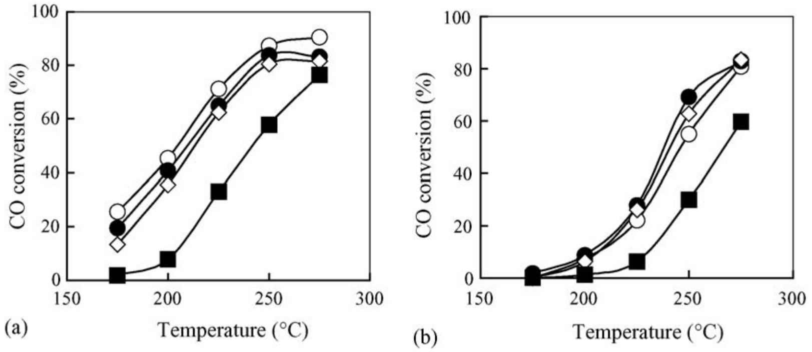

Fig. 1. Effect of impregnation sequence of Pt and Re on catalytic activities of Pt-Re catalysts: (a) Pt-Re/TiO_2 (R), (b) Pt-Re/ZrO_2, (●) Pt-Re, (○) PtRe, (◇) Re-Pt, and (■) Pt.