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Low-temperature water gas shift reaction over Pt–Re/TiO_2 catalysts prepared by a sub-critical drying method

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ABSTRACT

In order to prepare a highly dispersed Pt–Re/TiO_2 (R: rutile) catalyst with superior catalytic activity for the low-temperature water gas shift reaction (LT-WGS), the effect of the drying conditions after impregnation on the catalytic properties and activity of Pt–Re/TiO_2(R) catalysts was examined. As a result, sub-critical drying (SubCD), where the catalyst is dried under sub-critical conditions, was effective for the enhancement of Pt dispersion and for resisting Pt loss during the drying step. The SubCD catalyst prepared with $Pt(C_5H_7O_2)_2$ exhibited superior catalytic activity for LT-WGS at 250 °C compared with that of a commercial Cu/Zn catalyst.

1. Introduction

In the hydrogen production process by steam reforming of hydrocarbons for polymer electrolyte fuel cell (PEFC) systems, the water gas shift reaction at low temperature is (LT-WGS) used for the removal of CO, which deteriorates the Pt electrode of the PEFC. The authors reported that the Pt–Re/ZrO_2 and Pt-Re/TiO_2 (R: rutile) catalysts have superior catalytic activities for LT-WGS [1], and since then, Pt-Re catalysts have been paid much attention as candidates for new LT-WGS catalysts [2–5]. However, a reduction in the use of high-priced Pt by the improvement in the Pt dispersion is demanded.

The supported metal catalysts are conventionally prepared by evaporation to dryness. However, it is known that this method causes the migration of active metals with evaporation of the solvent, and this causes the growth and broad size distribution of metal particles. Recently, super-critical drying (SCD) has been investigated as a new method to obtain highly dispersed metal particles, compared with a conventional impregnation method [6]. Natachi and Igarashi reported that low-temperature super-critical drying with CO_2 as a fluid for SCD (LT-SCD) brought about the uniformly well-dispersed Ni particles over the Ni/SiO_2 and the LT-SCD catalyst showed higher catalytic activity for the hydrogenation of benzene than the catalyst prepared by a conventional thermal drying (TD) catalyst [7]. In addition, SCD is applied at high-temperatures using organic solvents (high-temperature super-critical drying; HT-SCD) for the preparation of supported metal catalysts, because the decrease in surface tension by the increased temperature results in highly dispersed metal particles. Sugita and Igarashi et al. have reported the well-dispersed Ni/SiO_2 catalyst, prepared by HT-SCD with cyclohexane, which exhibited higher catalytic activity than the LT-SCD and TD catalysts for the hydrogenation of benzene [8].

In this study, in order to prepare a highly dispersed Pt–Re/TiO_2 (R) catalyst with superior catalytic activity for LT-WGS, the effect of the drying conditions on the catalytic properties and activities of the Pt–Re/TiO_2 (R) catalysts was examined.

2. Experimental

2.1. Catalyst preparation

The TiO_2 (R) support was obtained by calcining JRC-TIO-6 (reference catalyst of the Catalysis Society of Japan) at 500 °C for 1 h in a stream of air. The impregnation of Re on TiO_2(R) was carried out prior to the impregnation of Pt. An ethanol solution of ammonium perrhenate was then added to the support powder. The Re concentration in the solution was adjusted to a Re loading of 0.67 wt.%. The mixture was evaporated on a water bath at 60 °C, and the resultant material was dried at 100 °C for 15 h, and then calcined at 500 °C for 1 h in a stream of air.

Subsequently, a toluene solution of bis (acetyl-acetonato) platinum (II) ($Pt(C_5H_7O_2)_2$) or platinum chloride hexa-hydrate ($H_2PtCl_6 \cdot 6H_2O$) was added to the Re/TiO_2(R) powder. The ratio of the amount of toluene to the pore volume of TiO_2 (0.5 cm^3/g) (solvent/pore volume ratio; S/P) was 1.6, 2.3, or 3.5. The Pt concentration

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in the solution was adjusted to a Pt loading of 1wt%. The impregnated sample was dried by thermal drying (TD; 100 °C, 0.1 MPa, 15 h), HT-SCD (200, 300, 350 °C, 20 MPa, 0.5 h), or sub-critical drying (SubCD; 150 °C, 20, 15, 3.0 MPa, 0.5 h). The fluid for HT-SCD and SubCD was pentane (Tc = 196.8 °C, Pc = 3.3 MPa). The dried sample was finally calcined at 500 °C for 1 h in a stream of air.

2.2. Activity test

LT-WGS was performed using a conventional fixed bed flow reactor, as previously described [9]. The space velocity (total) was 40,000 h^{-1}, and the mole ratio of H_2O to CO was 5.0. The feed gas was a quasi-reformed gas (CO: 10%, CO_2: 15%, H_2: 75%). For comparison, a commercial Cu/Zn catalyst (MDC-7; Süd-Chemie Catalysts) was used.

2.3. Characterization

The amount of CO chemisorbed on the catalyst reduced at 500 °C was estimated using a volumetric absorption apparatus (ASAP2010, Micromeritics) with a chemisorption unit, as previously described [9].

The Pt content in the catalyst was calculated from X-ray fluorescence spectroscopy (XRF; SEA 2010, Seiko) results, as previously described [10].

The Pt dispersion of the catalyst was calculated from the amount of CO chemisorbed on the catalyst reduced at 500 °C. The Pt dispersion was calibrated on the basis of the measured Pt content. The details of this procedure have been previously described [9].

Turn over frequency (TOF) for LT-WGS was calculated from the CO conversion at 250 °C and the amount of CO chemisorbed. The details of the procedure have been previously described [9].

Diffuse reflectance infrared Fourier transform (DRIFT) was performed using an infrared spectrometer (FTIR-8600, Shimadzu) with high-temperature DRIFT attachment (Spectra Tech). The resolution was 2 cm^{-1} and the accumulation was 256 counts. KBr was used as the reference material. The catalysts dried by TD and SubCD were measured at ambient temperature in a stream of N_2.

Table 1
Effect of S/P ratio on catalytic properties.[a]

Drying method	S/P ratio (–)	Pt content (%)	Amount of CO chemisorbed[b] (cm^3-STP/g-cat.)	Pt dispersion[b] (%)	Pt dispersion[b] (%)
HT-SCD	1.6	0.8	0.48	51.9	2.2
	2.3	0.8	0.43	46.3	2.4
	3.5	0.8	0.31	36.2	3.1
TD	2.3	1.0	0.51	46.8	2.4
	3.5	1.1	0.53	43.5	2.6

[a] 300 °C, 2.0 MPa.
[b] After reduction at 500 °C.

3. Results and discussion

3.1. Effect of drying conditions on the catalytic properties

Table 1 shows the effect of the S/P ratio on the catalytic properties. The HT-SCD catalyst prepared with lower S/P ratios showed relatively higher Pt dispersion. It can be considered that the excess solvent to pore volume caused the effusion of Pt precursor from the pores during the drying step, that is, a high S/P ratio resulted in a decline in the Pt dispersion. On the other hand, the effect of the S/P ratio on the Pt dispersion for the TD catalyst is less than that for the HT-SCD catalyst. This is because the Pt dispersion of the TD catalyst is not influenced by the initial amount of solvent because Pt is fixed onto the TiO_2 surface with the evaporation of solvent. In addition, Table 1 shows that the Pt content in the HT-SCD catalysts was less than the amount of Pt loaded in the catalyst (1 wt.%). This indicates the loss of Pt during the HT-SCD. From these results, it is apparent that HT-SCD causes the loss of Pt, although an increase in the Pt dispersion is achieved by adjusting the S/P ratio.

Table 2 shows the effect of drying temperature on the catalytic properties. For the catalysts prepared from $Pt(C_5H_7O_2)_2$, the amount of CO chemisorbed on the catalyst was increased with a lowering of the drying temperature. It is thought that an increase in the drying temperature causes the thermal sintering of Pt during the drying step. Among the catalysts examined, the SubCD catalyst prepared at 150 °C, which was the temperature below critical temperature for pentane (196.8 °C), exhibited the highest Pt dispersion. This result is contrary to the increase in the Pt dispersion expected by the removal of solvent via super-critical phase that prevents the condensation and/or effusion of metal by capillary action. In addition, Table 2 shows that the Pt content approached 1 wt.% by a lowering of the drying temperature below 200 °C, although the loss of Pt was observed at temperatures over 300 °C. It is thought that the high solubility of $Pt(C_5H_7O_2)_2$ in the SCD fluid caused the effusion of Pt. This result indicates that a lowering of the drying temperature is effective for resisting the loss of Pt during the drying step.

On the other hand, the effect of drying temperature on the catalytic properties of the catalysts prepared from $H_2PtCl_6 \cdot 6H_2O$ differed significantly from that for the catalysts prepared from $Pt(C_5H_7O_2)_2$. Table 2 shows that the amounts of CO chemisorbed on the HT-SCD and SubCD catalysts prepared from $H_2PtCl_6 \cdot 6H_2O$ were significantly lower than that on the TD catalyst, and the Pt content was also decreased by the HT-SCD and SubCD. This indicates that the effects of SubCD on the Pt dispersion and Pt content were greatly affected by the Pt precursor used.

Table 2
Effect of drying temperature on catalytic properties.

Drying method	Pt precursor	Drying temperature (°C)	Pt content (%)	Amount of CO chemisorbed[b] (cm^3-STP/g-cat.)	Pt dispersion[b] (%)
TD	$Pt(C_5H_7O_2)_2$	100	1.0	0.51	46.8
	$H_2PtCl_6 \cdot 6H_2O$		1.0	0.46	38.1
HT-SCD[a]	$Pt(C_5H_7O_2)_2$	350	0.8	0.37	42.5
		300	0.8	0.43	46.3
	$H_2PtCl_6 \cdot H_2O$		0.8	0.07	7.8
SubCD[a]	$Pt(C_5H_7O_2)_2$	200	1.0	0.48	40.6
		150	1.0	0.56	49.1
	$H_2PtCl_6 \cdot 6H_2O$		0.7	0.09	10.9

[a] 20 MPa, S/P ratio = 2.3.
[b] After reduction at 500 °C.