Preparation of Hydrophobic Platinum Catalyst in Supercritical Carbon Dioxide and Its Application for Isotopic Exchange Reaction of Hydrogen Atoms

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Abstract: The hydrophobic platinum catalyst for the chemical exchange reaction between water and hydrogen was prepared by the 2-step reduction of 1,5-cyclooctadiene dimethyl platinum (II): A reduction using the reducing agent of sodium tetraborohydrate solution in a water-in-CO₂ microemulsion and the autocatalytic reduction using hydrogen gas. The platinum particles were dispersed on the nano-textured hydrophobic layer formed on the gauze. Their average size was 46 ± 8 nm in diameter using a scanning electron microscope and energy dispersive X-ray spectroscopy. The hydrophobicity of the gauze did not decrease even after the deposition of the platinum nano-particles based on a measurement of the amount of water absorbed on the gauze. The hydrophobic platinum catalyst developed in this study was found to be effective for the isotopic exchange reaction of hydrogen atoms between hydrogen gas and water vapor containing deuterium.

Keywords: Hydrophobic, Platinum catalyst, Isotopic exchange reaction, Supercritical carbon dioxide

1. INTRODUCTION

The chemical exchange reaction of hydrogen atoms between hydrogen gas and water is effective to remove tritium from waste water discharged from nuclear facilities including fusion experimental devices and heavy-water cooled reactors [1]. This reaction consists of two steps. One is the vapor-water equilibrium reaction between liquid water and water vapor, and the other is the hydrogen isotopic exchange reaction between water vapor and hydrogen gas. For the latter, platinum particles are essential as a catalyst. The platinum particles are usually supported on hydrophobic materials thus keeping the platinum from being wetted by liquid water which covers the platinum particles and deactivates the catalyst. The Kogel catalyst which is made of styrene divinyl benzene copolymer (SDBC) was used as a hydrophobic platinum catalyst, however, it may cause the pressure drop and has flammable nature [1].

In the previous study, we have developed a novel catalyst using supercritical CO₂ [2]. The catalyst is made of the stainless steel gauze whose surface was covered with nano-textured layer to be hydrophobic [3]. For preparation of hydrophobic platinum catalyst, nano-sized platinum must be prepared and deposited in the nano-textured layer formed on the gauze to prevent the decline of the activity by wetting. To achieve this demand, the hydrophobic platinum catalyst was synthesized in supercritical CO₂ by two steps: 1) a reduction of 1,5-cyclooctadien dimethyl platinum (II) (CODMe₂Pt) by a reducing agent, sodium tetraborohydrate (NaBH₄) which was deposited on the nano-textured layer on the gauze with a water-in-CO₂ microemulsion, and 2) an autocatalytic reduction of CODMe₂Pt with hydrogen gas in supercritical CO₂. The surfactant system of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and F-pentanol can successfully form water-in-CO₂ (W/CO₂) microemulsion [4, 5] and CODMe₂Pt is very soluble in supercritical CO₂ [6]. The developed catalyst had the activity for the isotopic exchange reaction of hydrogen atoms between hydrogen and deuterium even in the presence of water.

In this study, the catalyst was applied for the isotopic exchange reaction of hydrogen atoms between hydrogen gas and water-vapor which is a main reaction of chemical exchange reaction between hydrogen and water for tritium removal. The hydrophobic platinum catalyst was prepared in the same manner as the literature [2] and the surface of catalyst was characterized by a measurement using a scanning electron microscopy (SEM) and an energy dispersive X-ray spectroscopy (EDS). For the evaluation of the activity of the catalyst, the fluid mixture of hydrogen gas and water-vapor which contained 4200 ppm of HDO was fed through the column where the catalyst was packed in advance. The concentration of HD in the hydrogen gas was measured using a stable isotope ratio mass spectrometer.

2. Experimental

2.1. Chemicals

The surfactant, AOT, and the precursor of platinum, CODMe₂Pt, were purchased from Sigma-Aldrich Co. The co-surfactant, 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (F-pentanol), and the reducing agent, NaBH₄ were obtained from Wako Pure Chemical Industries, Ltd. The liquid CO₂ cylinder was purchased from Japan Fine Products. The supported material, the gauze with a 6 mm in outer diameter and 6 mm in height was purchased from Tokyo Tokusyu Kanaami Co. Ltd. The surface of
the gauze was treated by chemical vapor deposition to make it hydrophobic by N koubou, Japan. The gauze was flattened and divided into 8 pieces as a specimen, since the cylindrical structure of the gauze might be affected to the measurement of the hydrophobicity. A piece whose hydrophobicity was confirmed was used as a support material. Ethyl alcohol (Wako Pure Chemical Industries, Ltd.) was used for the measurement of the hydrophobicity. The hydrogen gas (O_2 and CO_2 < 1 ppm) was purchased from Japan Air Gases Co. Ltd. The heavy water (99.9%) was obtained from Shoko Co. Ltd. All reagents were used without further purification.

2.2. Preparation of hydrophobic platinum catalysts

Fig. 1 shows a schematic diagram of the apparatus for the preparation of the hydrophobic platinum catalyst.

Carbon dioxide was fed into a high-pressure view cell (Taiatsu Glass Co. Ltd.) where 0.5335 g of AOT, 4.177 g of F-pentanol and 0.170 g of 0.1 mol.dm^{-3} NaBH_4 solution had previously been placed in advance, and then pressurized by the syringe pump (ISCO, 260D) at 25 MPa and 313 K. As a 1st step reduction, twenty pieces of the gauzes were placed in reaction cell A. Carbon dioxide and the additives were well mixed by a magnetic stirrer for 1 h to form the W/CO_2 microemulsion. After that, the valve between the high-pressure view cell and the reaction cell A was opened. The W/CO_2 microemulsion was contacted with the gauze for 40 min. Then the end valve of the reaction cell A was opened to depressurize and the gauze was collected. The collected gauzes and 10 mg of CODMe_2Pt were placed in reaction cell C and 2 MPa of hydrogen gas was pumped into reaction cell B. Both reaction cells were kept at 353 K. Carbon dioxide was introduced into the reaction cell C using the syringe pump and pressurized to 15.5 MPa for reduction of platinum by NaBH_4.

After 40 min of reduction, the fluid mixture of hydrogen and Sc-CO_2 in the reaction cell B was fed to the reaction cell C by syringe pump at 20 MPa. The auto catalytic reaction of CODMe_2Pt by hydrogen gas was conducted for 40 min as a 2nd step reduction. Finally, the end valve of the reaction cells B and C was opened to depressurize and the platinum supported gauze was collected. The gauze was well-washed by ethyl alcohol and distilled water for 4 times to remove the reagents.

2.3. Characterization of the catalyst

The surfaces of the gauzes were analyzed by a scanning electron microscopy (SEM, JEOL, JSM-6390AH) and an energy dispersive X-ray spectroscopy (EDS, JEOL, JED-2300HX). The hydrophobicity of the gauze was evaluated by the amount of water absorbed on the gauze. The gauze was placed into distilled water for a second, and then the gauze was placed into ethyl alcohol. The water content of ethyl alcohol was measured using a Karl-Fisher titrator (Hiranuma, AQ-7). The hydrophobicity was defined as the water absorbed in %:

\[
\text{Water absorbed, } \% = \frac{\text{Amount of water absorbed on gauze, } g}{\text{Mass of gauze, } g} \times 100. \quad (1)
\]

The measurements were repeated 10 times. The average and the standard deviation were calculated.

2.4. Measurement of the activity of the catalyst

Fig. 2 shows a schematic diagram of the apparatus used for the evaluation of the activity of the catalyst. This experimental apparatus was used to measure the activity of hydrogen-deuterium exchange between heavy water (HDO) and hydrogen gas over the catalyst. The apparatus consists of bed, humidifier and trap in two water baths. The concentration of HDO in water was 4200 ppm. The hydrogen gas was bubbled into the water and the heavy water saturated hydrogen gas was prepared using two-staged water vapor saturator. The fluid mixture of hydrogen gas and deuterium rich water-vapor was passed through a bed at 343 K where 20 pieces of the catalyst were placed to convert H_2 into HD by the reaction of H_2 + HDO = HD + H_2O. The flow rate of the fluid was controlled at 0.5 dm^3 min^{-1} by a mass flow controller. After the reaction, the fluid mixture was separated to gas and water by a cold trap and the gas was sampled. The molar concentration of HD in the gas was measured by the stable isotope ratio mass spectrometer (Finnigan, MAT252).

The activity of the catalyst was evaluated using k defined as follows.

\[
k = \frac{V}{H} \ln \frac{C_{\text{HDO}}^{\text{in}} - C_{\text{HDO}}^{\text{out}}}{C_{\text{HD}}^{\text{in}} - C_{\text{HD}}^{\text{out}}}, \quad (2)
\]

where \( V \) is the superficial gas velocity in cm s^{-1}, \( H \) is the height of the column in cm, \( C_{\text{HDO}} \) is the molar concentration of HD in the hydrogen gas in mol cm^{-3}. The superscripts e, in and out indicate the equilibrium composition, the feed composition and the sampling composition, respectively.
3. Results and discussion

The SEM images of the surface of the gauzes are shown in Figs. 3 (a), (b) and (c). Figs 3 (a), (b) and (c) indicate the surface of the gauze without hydrophobic layer, with hydrophobic layer, and with hydrophobic layer after the platinum deposition, respectively. The nano-textured hydrophobic layer was confirmed in Fig 3 (b), however, the surface of the gauze without hydrophobic layer was smooth shown in Fig 3 (a). It was confirmed that the platinum was deposited on the surface of the gauze shown in Fig 3 (c) by EDS analysis. Furthermore, the brightened particles were deposited on the surface of the gauze in Fig. 3 (c), which was not confirmed in Fig. 3 (b). The magnified SEM image of Fig. 3 (c) was shown in Fig. 4. The average size of these brightened particles were calculated to be 46 ± 8 nm.

The hydrophobicities of the gauzes were summarized in Table 1. The water absorbed (%) by the gauze without the hydrophobic treatment was 20 ± 9%. On the other hand, the water absorbed by the gauze with the hydrophobic treatment was 2.1 ± 0.8%, which was quite lower than that of the gauze without hydrophobic layer. The water absorbed by the gauze after the platinum deposition was 1.5 ± 0.4%. Both values for the gauze with the hydrophobic layer before and after the platinum deposition corresponded within the error limits. These results indicated that the hydrophobic layer was not destroyed and the hydrophobicity of the gauze had not decreased by the preparation of the catalyst.

The activity of the catalyst is shown in Fig. 5. The activity, $k$, was 21.0 at 5 min. It indicated that HD molecule was dissociated to hydrogen and deuterium atoms on the platinum and hydrogen isotopic exchange reaction was occurred. The hydrophobic platinum catalyst developed in this study was effective for the hydrogen isotopic exchange reaction even in the presence of water. However, the activity decreased to 10.4 after 60 min. The activity of the catalyst becomes constant if the active site in the catalyst does not change. It was considered that the deactivation of the catalyst was due to the absorption of water molecules on the surface of the platinum. As shown in Fig. 4, the size of platinum particles was 46 ± 8 nm in a diameter and some of them was existed on the upper surface of the hydrophobic layer. The size of microemulsion used in this study was about 6 nm [4]. So we thought that less than 6 nm of reducing agent could be dispersed on the hydrophobic layer and nucleation of platinum was able to achieve in the 1st step reduction. However, the platinum particles grew during the 2nd step reduction. As a result, the water molecules were absorbed on the surface of these particles. The deactivation by the absorption of water molecule was reported in the previous studies [7, 8]. The preparation of platinum catalyst using only the 1st step reduction is effective method to prevent the deactivation.

Fig. 4 The magnified SEM image of the surface of the gauze after the platinum deposition

4. Conclusion
The hydrophobic platinum catalyst for the chemical exchange reaction between water and hydrogen was prepared by the 2 step reduction of 1,5-cyclooctadiene dimethyl platinum (II): A reduction using the reducing agent of sodium tetraborohydrate solution in a water-in-CO₂ microemulsion and the autocatalytic reduction using hydrogen gas. The platinum particles were dispersed on the nano-textured hydrophobic layer formed on the gauze. Their average size of the particles was 46 ± 8 nm in diameter using a scanning electron microscopy. The hydrophobicity of the gauze did not decrease even after the deposition of the platinum nano-particles based on a measurement of the amount of water absorbed on the gauze. The hydrophobic platinum catalyst developed in this study was found to be effective for the isotopic exchange reaction of hydrogen atoms between hydrogen gas and deuterium-rich water vapor. The hydrogen and deuterium atoms were dissociated and exchanged with each other on the surface of the platinum particles and HD was generated.

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