Preparation of Hydrophobic Platinum Catalyst in Water-in-CO_2 Microemulsion for Chemical Exchange Reaction between Hydrogen and Water

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Platinum nano-particles were synthesized in a water-in-CO_2 microemulsion with two different surfactant systems. One of them was a mixture of sodium bis (2-ethylhexyl) sulfosuccinate and pentadecafluorooctanoic acid, and the other was a hydrocarbon surfactant polyoxyethylene (5) nonylphenyl ether. The nano-particles were deposited on the supported materials, polyethylene (PE) films, diatom earth and a stainless steel gauze with superhydrophobic treatment. The average diameter of the particles on the supported materials was measured to be less than 10 nm by transmission electron microscopy. The isotopic ratio of HD/D_2 increased by using the catalysts developed in this study. Under higher pressure conditions, the catalyst performance was improved when using the PE films. The platinum nano-particles deposited on the stainless steel gauze were also effective for the H_2-D_2 isotopic exchange reaction.

INTRODUCTION

The chemical exchange reaction of the hydrogen atom between hydrogen gas and water molecules is very effective for removing tritium from waste water discharged from nuclear facilities including fusion experimental devices and the heavy-water cooled reactors. For the chemical exchange between hydrogen gas and water molecules, platinum particles are essential as a catalyst. The platinum particle is usually supported on hydrophobic materials keeping the platinum from being wetted by liquid water.

One of the industrial methods for the preparation of the platinum nano-particles is using a water-in-oil microemulsion; small droplets containing a precursor of platinum are dispersed in organic solvents by a surfactant [1]. Recently, the utilization of carbon dioxide has been studied as an alternative medium to the conventional organic solvents [2-5]. Carbon dioxide is a desirable solvent because it is nontoxic, inexpensive and nonflammable.

To date, surfactants with fluorocarbon tails have been widely used to form a water-in-CO_2 microemulsion because the fluorinated compounds are highly soluble in dense CO_2. In previous studies [6-10], perfluoropolyether was used as a surfactant to form a water-in-CO_2 microemulsion with a stability of many hours. However, the fluorinated compounds are harmful, expensive and difficult to obtain compared with an ordinary surfactant.

In this study, platinum nano-particles were synthesized in a water-in-CO_2 microemulsion using two systems of surfactants. One was a mixture of sodium bis (2-ethylhexyl) sulfosuccinate (AOT) and pentadecafluorooctanoic acid (PFOA), and the other was a hydrocarbon surfactant, polyoxyethylene (5) nonylphenyl ether (NP-5). The fluorinated surfactant, PFOA, was less expensive and available. For use as a catalyst, the platinum particles were deposited on polyethylene (PE) films, a diatom earth for a GC sorbent and a stainless steel gauze by depressurization and then used as a catalyst for a hydrogen-deuterium (H_2-D_2) chemical exchange reaction. As for the gauze, we employed a special one whose surface was treated by chemical vapor deposition to become superhydrophobic. The catalyst performances for the isotopic exchange reaction between H_2 and D_2 were compared with Kogel catalysts which were used in a previous study [11].

I –EXPERIMENTAL

I – 1) Chemicals

The liquid CO_2 cylinder was purchased from Japan Fine Products. AOT was purchased from Aldrich. The fluorinated surfactant, PFOA, was obtained from Tokyo Kasei Kogyo Co., Ltd. The hydrocarbon surfactant, NP-5, was purchased from Wako Pure Chemical Industries, Ltd. The precursor of Pt, chloroplatinic (IV) acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), and a reducing agent, sodium tetrahydroborate ($NaBH_4$), were purchased from Wako Pure Chemical Industries, Ltd. Butyl alcohol (BuOH) was purchased from Aldrich. Polyethylene films (10 × 50 × 0.011 mm), a diatom earth for the GC sorbent (Gaschrom Q, GL Science, Inc.) and a stainless steel gauze wiht a 6 mm outer diameter and 6 mm height was used as the support of the platinum nano-particles. The surface of the gauze was treated by chemical vapor deposition to make it superhydrophobic. Kogel catalysts, whose platinum content was 0.8 wt%, were purchased from Showa Engineering Co., Ltd.

I – 2) Synthesis of platinum nano-particles

Figure 1 shows a schematic diagram of the high pressure apparatus used for the synthesis of the platinum nano-particles. The main parts consist of a high-pressure view cell with a 60 cm^3 inner volume, a syringe pump (ISCO, model 260D), a liquid CO_2 cylinder, a loading cell with a 1 cm^3 inner volume and a plunger pump (Nihon Seimitsu Kagaku, NP-KX-11). Liquid carbon dioxide was introduced into the high-pressure view cell where 0.74 g of AOT, 1.38 g of PFOA, 0.3 cm^3 of 50 mmol dm^{-3} (M) H_2PtCl_6 solution and supported materials had previously be placed in advance, and then pressurized by the syringe pump at 293 K. Supercritical carbon dioxide (SF-CO_2) was introduced into the high-pressure view cell where 0.87 g of NP-5, 0.06 cm^3 of 50 or 100 mM H_2PtCl_6 solution and supported materials had previously be placed, and then pressurized to 25 MPa, 308 K. The temperature of the cell was held constant by a water bath (EYELA, UA-10S). Carbon dioxide and the additives were well mixed by a magnetic stirrer until the water-in-CO_2 microemulsion was formed. The solution of $NaBH_4$ in BuOH was then fed from the loading cell to the high-pressure view cell. The concentration of $NaBH_4$ was 1.2 M in the AOT+PFOA system. After a 20-min reduction, the platinum nano-particles were deposited on the supported materials via the rapid expansion of the supercritical fluid solution using a restrictor with an inner diameter of 0.25 mm in the high-pressure view cell.

I – 3) Characterization of platinum nano-particles deposited on the supported materials

It is well-known that colloidal dispersions of metals exhibit absorption bands in the UV-vis region. These are due to the excitation of plasma resonances or interband transitions and are thus a characteristic property of the metallic nature of the particles. In this study, the absorption spectrum of the platinum nano-particles on the PE films in the AOT+PFOA system was measured using a UV-vis spectrometer (VARIAN, Cary 50) after the PE films were well-washed using ethanol and distilled water to remove the surfactant, reducing agent and H_2PtCl_6. The platinum particles deposited on the stainless steel gauze was observed by transmission electron microscopy (TEM, Hitachi, HF-2200).

I – 4) Measurement of hydrogen isotope ratio

The mixture gas of H_2 and D_2 was packed in an aluminum bag (Science Inc., AKK-30GL). The catalysts were placed in a stainless steel column. The mixture gas was fed into the stainless steel column at 0.1 $\mathrm{cm}^3 \cdot \mathrm{min}^{-1}$ using a mass flow controller (KOFLOOK, 3200-L). A hydrogen isotope ratio (HD/D_2, δ) in the mixture gas was measured using a quadrupole mass spectrometer (ANELVA, M-400QA-M). The catalyst performances for the chemical exchange reaction between H_2 and D_2 were evaluated by conversion in % defined as

$$\text{Conversion} = (\delta - \delta_f) / \delta_{th} \times 100 , \qquad (1)$$

where δ_f is HD/D_2 of the initial gas and δ_{th} is that of the equilibrium state which is 4.

The PE films were placed in a crucible and heated at 873 K using a furnace (Denken Co. Ltd., KDF-S80) for 20 min. The polyethylene films were decomposed into CO_2 and H_2O. The diatom earth was placed in a PTFE cell and dissolved with hydrofluoric acid at 398 K. The platinum nano-particles remained in the crucible and the PTFE cell were dissolved with aqua regia at 353 K for 15 min. The concentration of platinum in the solution was measured by the ICP-AES (Shimadzu, ICPS-7000).

II –RESULTS AND DISCUSSION

II –1) Synthesis of platinum nano-particles

The mixed solution of carbon dioxide and the additives became optically transparent for 30 min of stirring in the AOT+PFOA+liquid CO_2 and NP-5+SF-CO_2 system. The microemulsions consisting of reversed micelles with nanometers diameter are optically transparent because structures of this size are poor light scatterers. After introduction of the reducing agent, the microemulsions were colored gray within a few minutes. The supported materials were also colored gray after the deposition of the platinum nano-particles.

II –2) UV-vis measurement and TEM analysis of the platinum nano-particles

The absorption spectrum of the platinum nano-particles deposited on the PE films is shown in **Figure 2**. An absorption band appeared at 212 nm. Creighton *et al.* calculated the UV-vis absorption spectra of colloidal platinum particles based on the Mie theory and reported that the absorption band was at 215 nm [12]. The absorption band at 212 nm in Figure 2 seemed to be the plasmon absorption band of the platinum nano-particles.

Transmission electron microscopy was used to obtain an image of the platinum nanoparticles on the stainless steel gauze with superhydrophobic treatment. **Figure 3** shows the particles produced in the AOT+PFOA system. The size of the particles were less than 10 nm and they were dispersed on the nanotextured and hydrophobic layer. The particles in Figure 3 were counted in order to detrermine the size distribution. The diameter was 4.1 nm with a 1.7 nm standard deviation.

II –3) Catalyst performances for isotopic exchange reaction between H_2 and D_2

Table 1 lists the catalyst performances of the catalyst synthesized in the AOT+PFOA+liquid CO_2 at a different pressure, and 293K. The PE films were used as the supported materials. The conversion per 1 mg of platinum increases with an increase in the pressure. This can be explained by the fact that the molar fraction of CO_2 increases at higher pressures which lead to a decreased collosion frequency and then prevents the aggregation of the platinum nano-particles. Conversion with the catalyst synthesized at 19 MPa was 16.8%, which was the most effective for the isotopic exchange reaction between H_2 and D_2 in the AOT+PFOA system.

The catalyst performances of the catalyst synthesized in the NP-5+SF-CO_2 at 25 MPa, and 308K are listed in **Table 2**. Conversions with the catalysts synthesized with a 100 mM H_2PtCl_6 were 3.76, 2.24 and 11.2% when the reducing agent to H_2PtCl_6 ratio was 2, 4 and 6, respectively. Conversions with the catalysts synthesized with a 50 mM H_2PtCl_6 were 0.33, 0.73 and 1.09%. The catalyst performance was improved with an increase in the amount of the platinum ion and reducing agent in the NP-5+SF-CO_2 system.

Table 3 lists the catalyst performances of the platinum nano-particles deposited on the stainless steel gauze. The catalysts were synthesized using AOT+PFOA and NP-5. With AOT+PFOA, the catalyst was synthesized at 19 MPa. With the NP-5, the catalyst was synthesized using a 100 mM H_2PtCl_6 and 600 mM $NaBH_4$ solution at 25 MPa. Conversions were 19.8% with AOT+PFOA and 5.6% with NP-5. The catalyst synthesized in the AOT+PFOA system was superior to that in the NP-5 system. However, the amount of platinum ion dispersed in CO_2 were 0.015 mol with AOT+PFOA and 0.006 mol with NP-5 which lead to the differences of catalyst performance. It was considered that the conversion would improve by increasing the amount of the platinum ions. The hydrohobic catalysts synthesized in this study might be applied to the chemical exchange reaction of the hydrogen atom between the hydrogen gas and water.

CONCLUSIONS

The water-in-CO_2 microemulsion was prepared using two systems of surfactants, and both systems successfully prepared the platinum catalyst. Nano-particles were deposited on the supported materials, *i.e.*, the PE films, diatom earth and stainless steel gauze. The platinum nano-particles were found to be deposited on the supported materials on the basis of UV-vis measurements and TEM analyses. The catalyst performances were evaluated by an isotopic exchange reaction between H_2-D_2. The isotope ratio of HD/D_2 increased with the catalysts developed in this study. The platinum nano-particles deposited on the stainless steel gauze, with a superhydrophobic surface, might be applied to the chemical exchange reaction between hydrogen gas and water.

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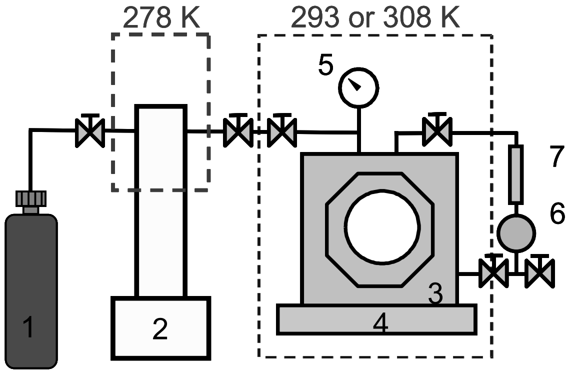

1: CO_2 cylinder, 2: Syringe pump, 3: High-pressure cell,
4: Stirrer, 5: Pressure gauge, 6: Plunger pump, 7: Loading cell

Figure 1 Schematic diagram of the apparatus for the synthesis of platinum nano-particles

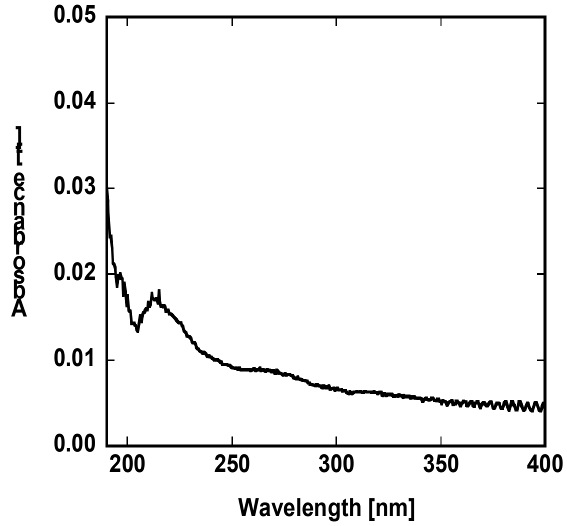

Figure 2 Absorption spectrum of platinum nano-particles deposited on the PE films

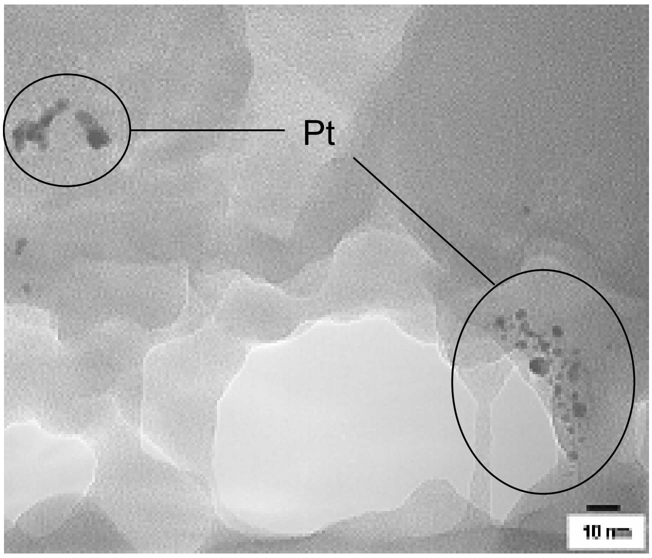

Figure 3 TEM image of platinum nano-particles deposited on the stainless steel

Table 1 Catalyst performances of catalyst synthesized with AOT+PFOA. The PE films were used as the support materials.

Pressure [MPa]	HD/D_2 ratio [-]	Pt content [%]	Conversion [%]	Conversion [%/1 mg Pt]
9	0.041± 0.001	5.8×10^{-3}	0.53	15
12	0.445± 0.026	6.8×10^{-2}	10.6	25
15	0.333± 0.016	4.7×10^{-2}	7.8	28
19	0.691± 0.017	4.4×10^{-2}	16.8	62
Kogel Catalyst	2.570± 0.077	8.0×10^{-1}	64	75
Blank (PE films)	0.019± 0.001	0	0	□

Table2 Catalyst performances of catalyst synthesized with NP-5. The diatom earth was used as the support material.

Pressure [MPa]	C_{Pre} [mM]	C_{Red} [mM]	HD/D_2 ratio [-]	Pt content [wt%]	Conversion [%]	Conversion [%/1 mg Pt]
25	50	100	0.025± 0.002	1.6×10^{-2}	0.33	3.2
		200	0.041± 0.001	1.7×10^{-2}	0.73	5.6
		300	0.056± 0.001	1.5×10^{-2}	1.09	11
	100	200	0.162± 0.010	1.3×10^{-2}	3.76	39
		400	0.102± 0.003	1.3×10^{-2}	2.24	26
		600	0.461± 0.006	3.8×10^{-2}	11.2	39
Kogel Catalyst	-	-	2.570± 0.077	8.0×10^{-1}	64	75
Blank (Diatom earth)	0	0	0.012± 0.001	0	0	-

Table 3 Catalyst performances of the staineless steel gauze.

System	Pressure [MPa]	Temperature [K]	HD/D_2 ratio [-]	Conversion [%]
AOT+PFOA	19	293	0.814± 0.011	20
NP-5	25	308	0.258± 0.015	6
Kogel Catalyst	-	-	2.570± 0.077	64
Blank (Gauze)	-	-	0.019± 0.002	0