Synthesis of Super-hydrophobic Platinum Catalyst

Based on a Supercritical CO_2 Platform

Y. Enokida*, K. Sawada, and K. Hayashida

EcoTopia Science Institute, Nagoya University, 1 Furo-cho, Chikusa-ku, Nagoya 4648603, Japan

E-mail yenokida@nagoya-u.jp, Fax +81 52 789 5936

A super-hydrophobic platinum-catalyst for hydrogen-atom exchange-reaction between a diatomic hydrogen molecule and a water molecule was synthesized using a series of procedures in supercritical CO_2. Firstly super-hydrophobic surface layer was prepared onto a gauze of stainless steel by a sol-gel reaction utilizing water-in CO_2 micro-emulsion containing silicon and titanium alcoxides being followed by deposition of platinum nanoparticles through capillary condensation in tiny spaces in the super-hydrophobic layer of platinum precursor being dissolved in supercritical CO_2 and heat treatment at 500 K. The hydrogen-atom exchange-reaction between a diatomic hydrogen gas molecule and a water molecule was confirmed by using radioactive tritiated hydrogen. The tritium atom (T) was transferred into a water molecule as HTO by contacting with the super-hydrophobic platinum catalyst synthesized by the method described-above in a supercritical CO_2 platform. This catalyst can be used directly for waste water treatment in the nuclear facilities such as nuclear fusion experimental reactors or deutriated water moderated nuclear fission reactors.

INTRODUCTION

Platinum nanoparticle works well as a catalyst for an exchange reaction of hydrogen atoms between diatomic hydrogen gas molecules and water molecules in gas phase, which is a very important step for tritium concentration through a combined process consisting of a chemical electrolysis and a chemical exchange, (i.e. CECE process).[1-2] In this isotopic exchange-process, platinum particles should not be covered with liquid water so that they are usually deposited on hydrophobic surfaces, for which plastics such as styrene divinyl benzene copolymer have been employed. But plastics are burnable so that a safety concern with treating radioactive tritium is paid seriously for the hypothetical accident where abnormal air may invade into the isotopic exchange column and the plastics support be in combustion. Another disadvantage of the current plastic support is a relatively large pressure-drop caused in a packed column, because shape of the current plastic support is spherical and so tends to be closely packed together. In the packed column currently used Dixon gauze rings of stainless steel are also employed for isotopic exchange reaction of hydrogen atoms between water molecules in gas and liquid streams. The gauze rings are expected to offer a large surface-area for the isotopic exchange reaction. The rings are made of stainless steel and not combustible. They have many pores and pressure drop is much smaller than the spherical

plastic support. Therefore our proposal is depositing platinum nanoparticles on the stainless steel gauze for the catalyst. The surface of the stainless steel is, however, hydrophilic, a platinum nanoparticle is easily wet by a cluster of water molecules, i.e. liquid water, and this is not good for a catalyst support.   In order to overcome this technical problem we have performed an attempt that super-hydrophobic surface layer[3-14] was prepared onto the surface of stainless steel gauze by a sol-gel reaction in supercritical CO_2. The second technical challenge was deposition of platinum nanoparticles in the super hydrophobic surface-layer, for which we have applied capillary condensation[15] of supercritical CO_2 containing platinum precursor occurred in tiny spaces in the hydrophobic surface layer. The two processes of preparations of the super-hydrophobic layer and deposition of platinum particles are serially performed in supercritical CO_2. In the present paper we describe the experimental methods and results for these two processes and the performance of the prepared super-hydrophobic platinum catalyst for the hydrogen-atom exchange-reaction for tritium concentration using the radioactive hydrogen.

MATERIALS AND METHODS

Formation of super-hydrophobic surface layer on stainless steel gauze

The formation of the super-hydrophobic layer was experimentally attempted by the three steps as follows; i) solvation of silicon and titanium alcoxides in supercritical CO_2, ii) gelation with using water in supercritical CO_2 micro-emulsion, and iii) plating of CF_3 terminating compound in supercritical CO_2. An experimental set-up illustrated in **Figure 1** was employed for each of the three steps.
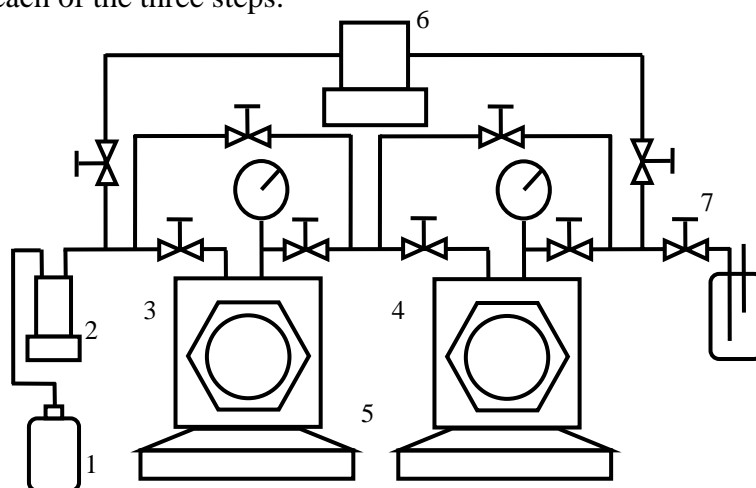

Figure 1. A schematic diagram of the experimental set-up for the preparation of super-hydrophobic surfaces.

1. Liquid CO_2 Cylinder, 2. Syringe Pump(D-260, ISCO, U.S.A.), 3. High-Pressure Vessel A(SCF-S, Taiatsu Glass Corp., Japan), 4. High-Pressure Vessel B(SCF-S, Taiatsu Glass Corp., Japan), 5.Magnetic stirrer base (RCX-1000S, EYLA, Japan), 6. Circulating Pump(NP-KX520,

Nippon Seimitsu Kagaku, Japan), 7 . Back-Pressure Regulating Valve(SFC-BPG, JASCO, Japan).

Prior to the experiment, Dixon gauze rings of 6 mm in diameter (Tokyo Kanaami Corp., Japan) were placed in the vessel A. The capacity of the vessel was 60 cm^3 and the number of placed rings were approximately 100. For the first step, tetraethyl orthosilicate (TEOS) (Wako Pure Chemical Industries, Japan, Special reagent grade), and tetraethyl orthotitonate (TEOT) （Sigma Aldrich, Japan, Reagent grade） were placed in the vessel A. The two reagents were well dissolved in supercritical CO_2 at 40 degrees C and 25 MPa. The concentrations of TEOS and TETO in CO_2 were 3.6×10^{-4} mol dm^{-3} and 3.3×10^{-4} mol dm^{-3}, respectively. In the second step, a water in supercritical CO_2 micro-emulsion was prepared in the vessel B with using ultra pure water and a surfactant system, for which Bis(2-ethylexyl)-sulfosuccinate sodiumsalt(AOT)(Sigma Aldrich, Japan, Purity 98%）+2,2,3,3,4,4,5,5-Octafluoro-1-Pentanol (F-pentanol) (Wako Pure Chemical Industries, Japan, Reagent grade) or Tergitol$^®$ TMN-3 (TMN-3) （Fluka, Japan, Purity 100%）. The internal fluid of the vessel B was introduced into the vessel A by using the circulating pump and sol-gel reaction was initiated. The reaction duration was 3 hours being followed by decreasing pressure by 0.5 MPa min^{-1} up to the atomospheric pressure.

In the third step, perfluorooctyl triethoxysilane(POTS) (Sigma Aldrich Japan, Japan, Reagent grade) was disolved in supercritical CO2 at 40 degrees C and 25 MPa in the vessel B and introduced into the vessel A to contact with the dixon gauze rings for which surface layer was already deposited in order to plate the POTS. The concentration of POTS in CO_2 was 2.0 % in weight. The plating time was one hour being followed by decreasing pressure by 0.5 MPa min^{-1} up to the atomospheric pressure. Finally the treated Dixon gauze rings were heated in a tubing furnace at 150 degrees C for 2 hours in order to remove water and excess amount of POTS. The surface layer of the rings were observed with a scanning electron microscope with a feature of Energy dispersive X-ray spectroscopy(JSL-7600F, JEOL, Japan), and water contact angle was measured by the $\theta / 2$ method.

Deposition of platinum nanoparticles on the super-hydrophobic layer

The same experimental set-up as is illustrated in **Figure 1** was utilized to deposit platinum nanoparticles on the super-hydrophobic surface on the stainless gauze rings. As a platinum precursor, dimethyl (1,5-cyclooatadiene) platinum(II) (CODPtMe2) (Sigma Aldrich Japan, Japan, 98% in purity) was placed in Vessel B and dissolved in supercritical CO_2 at 80 degrees C and 25 MPa. The concentration of the Pt precursor was 0.2% in molecular fraction. Then the CO_2 containing Pt precursor was transferred at 80 degrees C and 25 MPa, into vessel A , in which the stainless gauze rings were placed. The contacting time was 3 hours and the rings were heated at 120 degrees C in a tubing furnace (ARF-30K, Asahi Science Corp., Japan) for 3 hours in order to form Pt particles.

Evaluation of catalytic activity of the prepared catalyst

An evaluation of catalytic activity of the prepared catalyst was performed by using an experimental system illustrated in **Figure 2**. In a moisturizer (4), tritiated water was placed and hydrogen gas was fed from a gas cylinder (1) in order to obtain hydrogen gas saturated

with water vapour, where heaviest hydrogen isotope exist as tritiated water form (HTO) in gas phase. In the isotopic exchange column (6), the prepared catalysts in this study, i.e. platinum particles supported on the super-hydrophobic Dixon gauze rings were packed and contacted with the hydrogen gas saturated with tritiated water vapour. In the column, the following isotopic exchange reaction was expected to occur.

$$HTO + H_2 \leftrightarrow H_2O + HT \tag{1}$$

The residual HTO was trapped in liquid water in the vessel(7). HTO concentration was measured by radioactivity with using a low-background liquid scintillation counter (LSC-LB1, ALOKA Corp., Japan). By comparing specific radioactivity of water specimen from vessel (7) with that from moisturized (4), completion degree of reaction described by Eq.(1) was evaluated. The evaluation was based upon the following equation.

$$\eta = \frac{y_0 - y}{y_0 - y_e} \tag{2}$$

where y_0 is a concentration of HTO in water vapour before contacting with the catalysts, y, a concentration after contacting, y_e, theoretical value at the equilibrium state, which was given in the literature[2].
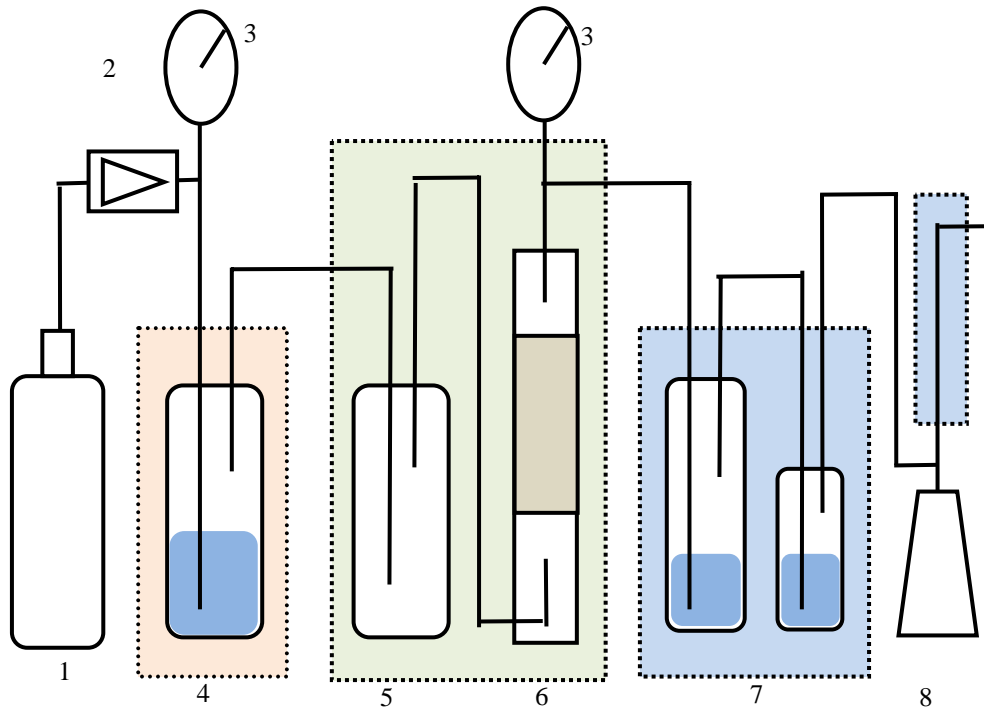

Figure 2 A schematic diagram of the experimental set-up for the evaluation of catalyst performance.

1. Hydrogen cylinder, 2. Mass flow controller, 3. Pressure gauze, 4 Moisturizer, 5. Entrainment trapping vessel, 6. Isotopic exchange column, 7. Tritium recovery water vessel, 8. Final trapping water vessel

RESULTS

Formation of super-hydrophobic surface layer on stainless steel gauze

Figure 3 shows an example of photo taken by a scanning electron microscope foe the treated surface of the Dixon gauze rings in supercritical CO_2.   Many spherical particles of sub-micrometer in diameter were deposited on the stainless steel surface. According to the surfactant systems employed, different size distribution of particles of SiO_2 and TiO_2 were observed, and averaged sizes are shown in **Table I** where w values, which is defined as a molecular ratio of surfactant to water, were shown, too.   **Figure 4** successfully shows hydrophobic characteristic of the prepared surface. The water drop contact angle was 147 degrees.   This is the first successful attempt to prepare a super-hydrophobic layer in CO_2 platform as far as we know.
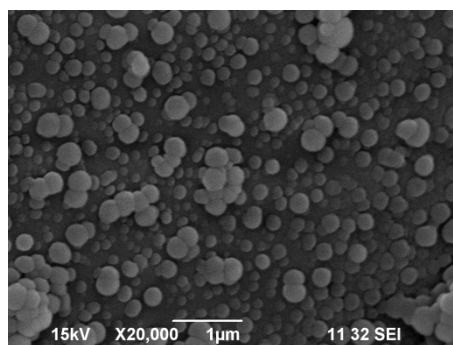

Figure 3 A photograph of the prepared surface imaged by a scaning electron microscope.

Figure 4 A droplet placed on the prepared layer.

Table I Averaged size of formed SiO_2 and TiO_2 particles on the Dixon gauze rings for different surfactant systems in CO_2

Surfactant system	Averaged diameter (micrometer)
AOT+F-pentanol	1.07-1.26 (w=5 to 8)
TMN-3	0.27(w=2)

Deposition of platinum nanoparticles on the super-hydrophobic layer

A photograph for platinum particle deposited on the super-hydrophobic surface layer by a transmission electron microscope (TEM) is sown in **Figure 5(a)** and a result of energy dispersion x ray spectrometry (EDS) for the particle is shown in **Figure 5(b)**. The averaged diameter of the Pt particle was approximately 2 nm.
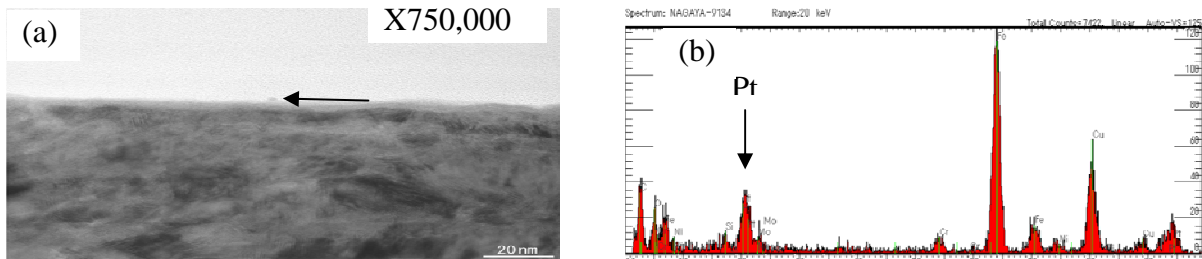

Figure 5(a) TEM photograph of the deposited surface and **(b)** a result of EDS.

Evaluation of catalytic activity of the prepared catalyst

The catalytic performance evaluated using Eq. (2) in our experiment was 0.91 ± 0.05. This value shows enough performance as hydrogen isotopic exchange catalyst.

CONCLUSION

A super-hydrophobic platinum-catalyst for hydrogen-atom exchange-reaction between a diatomic hydrogen molecule and a water molecule was successfully synthesized using a series of procedures in supercritical CO_2. The prepared catalyst is made of no combusting materials and then can be used directly for waste water treatment in the nuclear facilities such as nuclear fusion experimental reactors or deutriated water moderated nuclear fission reactors with inherent safer feature rather than catalysts on plastics supports.

REFERENCES :
[1] ARITA, T., et al., Fusion Technology, Vol. 30, **1996**, p. 864
[2] SUGIYAMA, T. et al., Fusion Eng.Des., Vol. 81, **2006**, p.833
[3] ONDA, T. *et al. Langmuir*Vol. 12, **1996**, p.9
[4] LAU, K.K.S. *et al.*, *Nano. Lett.* Vol. 3, **2003**, p. 1701
[5] FENG, L. *et al.*, *Adv. Mater*, Vol.16, **2004**, p.302
[6] HE, B. *et al.*, *Langumuir*, Vol.19, **2003**,p.4999
[7] SU, C. *et al.*, *Appl. Surf. Sci.*, Vol.253, **2006**, p.2633
[8] YANG, H. *et al.*, *J. Coll. Inter. Sci.* Vol.325, **2008**, p.588,
[9] ZHANG, J. L. *et al.*, *Macromol Rapid Commun* Vol. 25**, 2004**, p.1105
[10]SHIU, J. Y. *et al.*, *Proc. SPIE-The International Soc. Optical Engineer.* Vol. 5648, **2005**, p.325
[11] YABU, H. *et al.*,*Chem Mater*, Vol.17, **2005**, p. 5231
[12] FENG, L.*et al.*, *Nano. Lett.* Vol. 3**, 2003**, p. 1701
[13] HE, B.*et al.*, *Langmuir*, Vol. 19, **2003**, p. 3432

[14] YOUNGBLOOD, J. P. *et al., Macromolecules* , Vol.32, **1999,** p.6800

[15]GELB, L. D., *REPORTS ON PROGRESS IN PHYSICS*, Vol. 62, **1999**, p. 1573