# Preparation of Activated Carbon Cloth Supported Platinum Catalyst Using Supercritical Carbon Dioxide

Atsushi SHONO*, Miki FUKAWA, Mitsuo KOYAMA, Yasukazu SAITO,
Shinya HODOSHIMA and Katsuto OTAKE

Department of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science,
12-1 Ichigaya Funakawara-machi, Shinjuku-ku, Tokyo, 162-8601, JAPAN
* To whom correspondence should be addressed.
E-mail : ashono@ci.kagu.tus.ac.jp, Fax : +81-3-5228-8316

A new simple method for preparation of activated carbon cloth supported platinum catalyst was proposed using supercritical carbon dioxide ($scCO_2$) as a medium. Platinum (II) acetylacetonate was used as a precursor in this study. The proposed method is consists of two processes, namely impregnation of the precursor by $scCO_2$ and reduction of the precursor. To evaluate the activity of the catalyst, dehydrogenation of decalin under superheated liquid film condition was employed. Effects of impregnation temperature, impregnation pressure, reduction temperature and reduction time on the catalyst activity were investigated.

## INTRODUCTION

Recently, a novel method for the preparation of nanocomposite of noble metal nanoparticles and polymers which uses supercritical carbon dioxide ($scCO_2$) as an impregnation solvent of metal precursors was proposed. Yoda *et al*. reported the preparation of a Platinum and Palladium/Polyimide nanocomposite film with the method [1]. Compared with the ordinal methods that uses liquid solvents, the method has several advantages such as i) simplicity of processes, ii) impregnation into micropores, and iii) reduction of metal precursors without reductants. In this study, preparation of activated carbon cloth supported platinum catalyst (Pt/ACC) for dehydrogenation of chemical hydrides was studied. Effects of impregnation temperature, pressure, and reduction conditions of metal precursors on the size and the activity of the catalyst were investigated.

## EXPERIMENTAL

Platinum(II) Acetylacetonate, $Pt(acac)_2$, was used as the catalyst precursor without further purification. Thermal stability of the precursor was measured by TG/DTA analysis. As

the catalyst support material, activated carbon cloth (ACC, BET specific surface area: $1.8x10^3$ $m^2/g$, average pore size: 1.5 nm, Kuraray Chemical Co.) was used.

Schematic diagram of $scCO_2$ apparatus is shown in Figure 1. An ACC disk of 3 cm in diameter and 0.8 mm in thickness was set into a high-pressure cell with $Pt(acac)_2$, and $scCO_2$ was loaded into the cell. Impregnation was carried out at 50 – 150 $^oC$ and 10 - 25MPa for 24 h. After the impregnation step, the precursor impregnated in the ACC was thermally decomposed at 100-300 $^oC$ and at atmospheric pressure in $CO_2$, $N_2$ or $H_2$ for 0.5 - 6h.

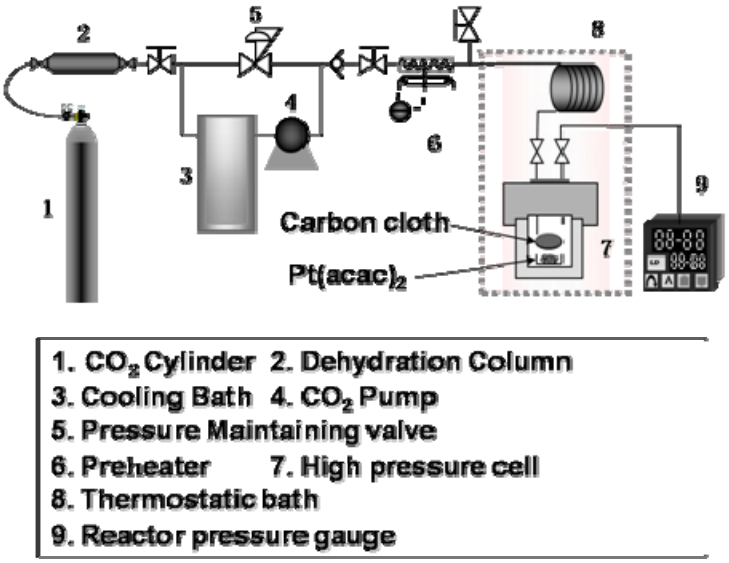



Figure 1 Experimental apparatus for catalyst preparation using $scCO_2$ system

Morphology of the prepared catalysts was observed by TEM and SEM. Platinum content of the catalyst was determined by ICP-AES analysis. Activity of the catalyst was evaluated by measuring decalin dehydrogenation in a batch-wise reactor (flat bottom flask, 50 ml). Experimental setup is shown in Figure 2. Reaction was performed at atmospheric pressure at 210 $^oC$, and refluxing temperature was 5 $^oC$. The amount of decalin to the catalyst (5 wt% Pt/ACC, 0.11g) was fixed to 0.4 mL, which was optimized in preliminary experiments. Evolved hydrogen was collected and measured with a gas burette. The catalyst activity was evaluated decalin conversion at 2.5h.

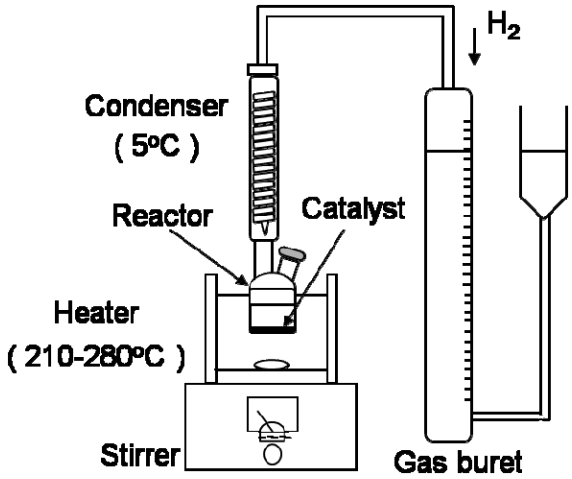


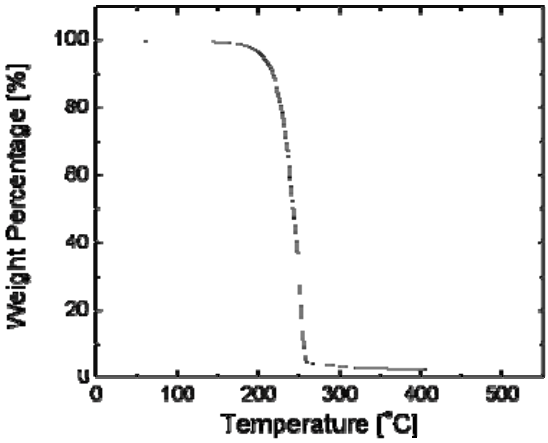

Figure 2 Experimental setup for catalytic hydrogen evolution from decalin under reactive distillation conditions in a batch-wise operation

## RESULTS AND DISCUSSION

### Thermal Stability of $Pt(acac)_2$

To determine the maximum temperature for impregnation, thermogravimetric

analysis of $Pt(acac)_2$ powder was carried out. The result is shown in Figure 2. The weight of the $Pt(acac)_2$ started to decrease at around 200°C, and decomposition completed at 260°C. From the result, in this study, the impregnation temperature was determined from 50 to 150 °C.

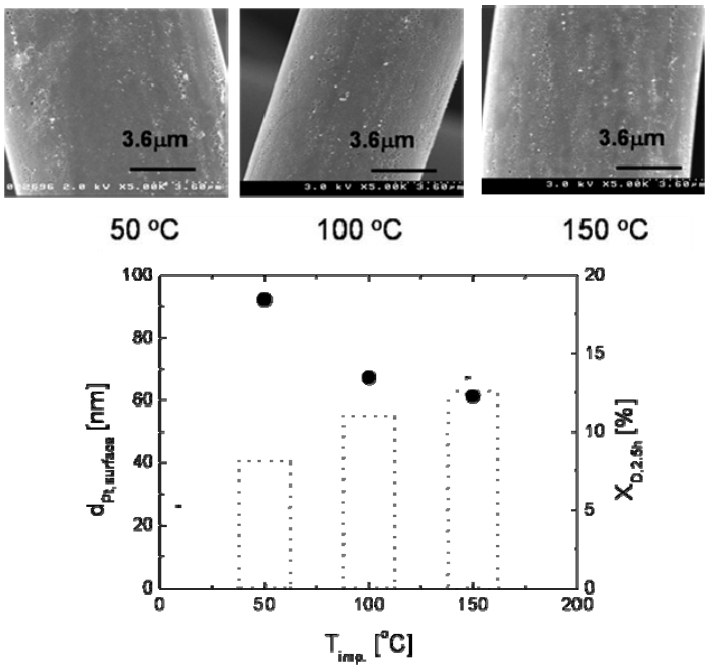



**Measurement Conditions**
$N_2$ flow ( flow rate : 50ml/min)
Temperature rising rate: 5 °C/min
Temperature range : 25 °C - 500°C

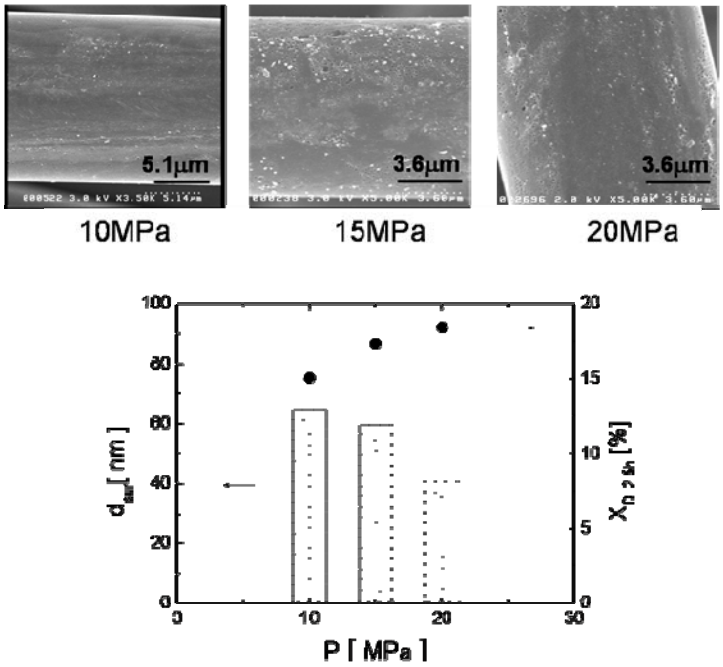
Figure 3 Thermal stability of the precursor

**Effect of Impregnation Conditions on the Platinum Deposition and the Catalytic Activity**

Effects of impregnation temperature and pressure on the deposition of Pt particles and the catalytic activity of dehydrogenation were examined, and the results are shown in Figure 4 (a) and (b), respectively. From SEM images shown in Figure 4 (a) and (b), it could be found that small particles ranging from 40 to100 nm in diameter were deposited on the surface of the ACC support. SEM-EDX analysis indicated that these particles are platinum. Effect of impregnation temperature on the deposited Pt particle size at constant $CO_2$ pressure (20MPa) is shown as the histogram in Fig.4 (a). The average diameter of the particles is increased with increasing the temperature. In contrast, the average diameter of the Pt particles is decreased with increasing in pressure as shown in Fig.4(b). To evaluate the activity of the prepared Pt catalyst, decalin dehydrogenation reaction was carried out. The conversion of decalin dehydrogenation reaction at 2.5h, $X_{D,2.5h}$, is also shown in Figs.4 (a) and (b) as closed circles. The decalin conversion is decreased with the increase in the surface deposited Pt particle diameter. Cross sectional TEM images of the PT/ACC are shown in Figure 5. The large Pt particles are observed in the surface layer, and relatively mono dispersed small Pt particles of 2.3 nm in average diameter are distributed inside the carbon fiber. The diameter of the Pt particles had no significant dependence on the impregnation conditions. It was also found that the total amount of platinum estimated from the number and diameters of Pt particles deposited on the ACC surface is 10% less than that determined by ICP-Analysis for all Pt/ACC catalysts prepared in this study. The obtained results suggest that the small Pt particles inside the ACC fiber act as major catalyst for dehydrogenation. It is also seems to suggest that the increase of catalyst activity with decreasing the diameter of the large Pt




(a) Effect of impregnation temperature at 20MPa




(b) Effect of impregnation pressure at 50°C

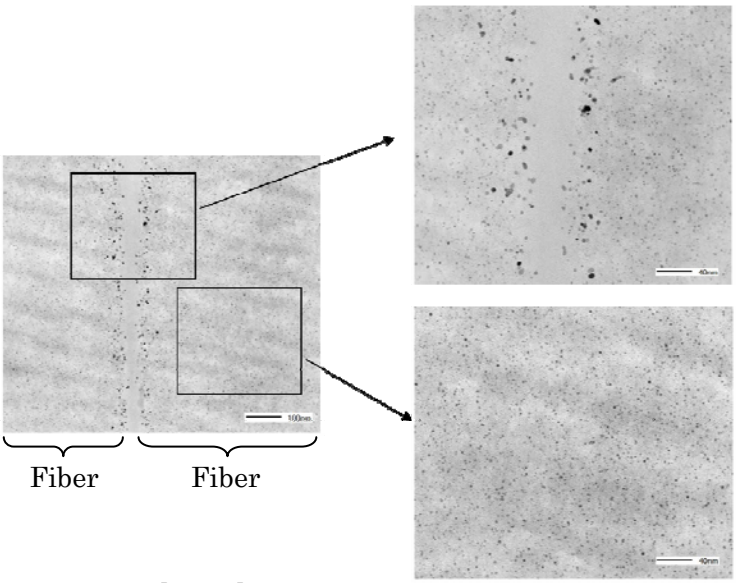
**Catalyst preparation** $Pt(acac)_2$ impregnation for 24h and Reduction at 200°C for 2h under $CO_2$ flow (10mL/min). Support : Activated carbon cloth

**Dehydrogenation of Decalin** Catalyst: Carbon cloth-supported platinum particles (Pt/C, 5 wt%), Amount ratio of catalyst to reactant: 0.1 g / 0.4 ml (superheated liquid-film state), Reaction conditions: Boiling and refluxing by heating at 210°C and cooling at 5°C for 2.5 h

Figure 4 Effects of impregnation conditions on catalyst activities

particles on the surface is due to the increase in the number of the small Pt particles inside the ACC, namely due to the increase in the catalyst surface area per unit volume.

The effects of impregnation temperature and pressure on the activity of the Pt/ACCs are explained as follow. The density of the $scCO_2$ increases at high pressures and low temperatures, yielding the solubility of precursor increase [1]. As a result, the precursor diffused deeply into the mesopores of the ACC fiber, and the pores prevent the aggregation of Pt nanoparticles during the reduction processes. Furthermore the percentage of thermally decomposed precursor during the impregnation process will increase with the increase in temperature, since the impregnation temperature approaches to the precursor decomposition conditions shown in Figure 3. Thus, in the impregnation at high temperatures, the precursor decomposed and aggregated into the large particle on the surface instead of diffusing inside of the ACC fiber.




**Experimental Conditions**
Support : Activated Carbon Cloth, Precursor : $Pt(acac)_2$
$Pt(acac)_2$ Impregnation at 50°C and 20MPa for 24 h in $scCO_2$ system
Reduction of $Pt(acac)_2$ at 200°C and 0.1MPa for 2h under $CO_2$ atmosphere

Figure 5 TEM images of activated carbon cloth supported Pt catalyst

**Effects of reduction conditions on the platinum deposition and the catalytic activity**

The effect of reduction conditions, such as reduction time, temperature, and the kind of flow gas, on the catalytic activity was investigated. The catalytic activity was evaluated using the decalin conversion at 2.5 hours. Results are shown in Table 1. For gases examined in this study, it was

Table 1 Effects of Reduction conditions on the catalyst activitis

| Reduction System | Temperature [°C] | Time [h] | Decalin Conversion at 2.5h [%] |
|---|---|---|---|
| $H_2$ | 200 | 0.5 | 7.7 |
| | | 1 | 7.1 |
| | | 6 | 5.8 |
| | 300 | 0.5 | 4.5 |
| | | 1 | 7.1 |
| | | 6 | 10.1 |
| $N_2$ | 200 | 2 | 15.5 |
| | | 4 | 16.0 |
| | 270 | 2 | 16.1 |
| $CO_2$ | 200 | 2 | 18.4 |
| | | 4 | 16.8 |

found that the reduction time more than 1 hour and the reduction temperature higher than 200$^{o}$C show no significant effects on the catalytic activity.

As shown in Table 1, the activity of the catalyst reduced under $H_2$ is lower than that reduced under $CO_2$ or $N_2$. This might be due to the slow degradation and reduction of the metal precursors under the inert gases that will prevent the aggregation of the metals. On the other hand, for the case of $H_2$, the Pt metal particle produced by the rapid reduction absorbs $H_2$ to attract the precursor to form the larger particles. In other words, Pt particles act as catalyst for Pt aggregation to form the larger particles [3].

## CONCLUSION

Catalyst of high activity for the dehydrogenation of the organic hydrides was prepared with using supercritical impregnation of metal precursors to the ACC and successive reduction under inert gas conditions. The effects of impregnation conditions on the activity of the catalyst were examined. It was found that the activity of the Pt/ACC catalyst prepared at higher pressures and lower temperatures, or the higher densities, of the impregnation conditions has higher activities. The high activity of the catalyst was partly due to the impregnation of metals into the mesopores of the ACC. The effectiveness of the reduction under $CO_2$ atmosphere was also revealed.

## REFERENCES

[1] Satoshi Yoda, Atsushi Hasegawa, Hiroyuki Suda, Yuko Uchimaru, Kenji Haraya, Tomoya Tsuji, and Katsuto Otake, Chem. Mater., **2004**, 16 (12), pp 2363 - 2368

[2] Shinya Hodoshima, Atsushi Shono and Yasukazu Saito, Energy Fuels, **2008**, 22 (4), pp 2559 - 2569

[3] James J. Watkins and Thomas J. McCarthy, Chem. Mater., **1995**, 7 (11), pp 1991 - 1994