Fabrication of Polymer Film Immobilizing Pd Nano Particles by Plasma-Assisted Method and Evaluation of its Catalytic Activity

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We describe the development of a novel palladium catalyst supported on a durable hydrophilic surface fabricated by the plasma-assisted method. Pd nano particles were immobilized on the polymer film possessing a durable hydrophilic surface (LDPE-Pd film). Two kinds of LDPE-Pd film possessing different Pd density were prepared to estimate the chemoselective hydrogenation. Stilbene and 4-nitroaniline were readily hydrogenated with LDPE-Pd film, indicating that the temperature and density of Pd on film might be very important for chemoselectivity.

Keywords: Pd nano particle, Plasma irradiation, Hydrophilic polymer surface

1. Introduction

The development and implementation of reusable catalysts in organic chemistry is becoming more important with increasing environment awareness and the current focus on green chemistry initiatives. Transition metal, such as Pd, Rh and so on, has been used as a catalyst to hydrogenate various functional groups. Development of chemoselective hydrogenation is one of the most important topics in organic chemistry. Recently, it has been reported that the chemoselective hydrogenation can be achieved by using palladium catalyst supported on various type of support, such as molecular sieves, ceramics, resin and so on [1-4]. Chemoselectivities of these palladium catalyst are considered to be derived from the character of the catalyst support.

In a previous paper, we synthesized the polymer film immobilizing Au nano particles by the use of a durable hydrophilic surface fabricated by the plasma-assisted method [5]. The schematic illustration for the fabrication of durable hydrophilic surface is shown in Fig. 1 [6-9]. This method involves sorption of methylvinylether-maleic anhydride copolymer (VEMA) into the surface layer of low density polyethylene (LDPE) and immobilization by a plasma-assisted cross-link reaction. Hydrolysis of VEMA follows to generate carboxyl groups on the surface. The durable hydrophilic surface thus introduced has been confirmed by not only the measurement of water contact angle but also demonstration of long term stability of surface lubricity on the urethane-made catheter. The durable hydrophilic surface can make several bio-application works [10-16]. To increase the content of carboxyl groups, VEMAC was introduced on the LDPE-VEMAC film with hexamethylenediamine (HMDA) as a spacer, and then Au nano particles was immobilized on this film via 2-aminoethanethiol. The oxidation of benzyl...
alcohol was performed with the film immobilizing Au nano particles in a basic aqueous solution.

In this paper, we describe the development of a novel palladium catalyst supported on a durable hydrophilic surface fabricated by the plasma-assisted method. Pd nano particles were immobilized on the polymer film possessing a durable hydrophilic surface (LDPE-Pd film). Two kinds of LDPE-Pd film possessing different Pd density were prepared to estimate the chemoselective hydrogenation. The hydrogenation activity of LDPE-Pd films was evaluated with stilbene and 4-nitroaniline in methanol.

2. Experimental

2.1. Preparation of LDPE-VEMAC film

LDPE film was prepared by cutting a bag made of polyethylene (UNI-PACK E-4, thickness 0.04 mm) purchased from Seisannipponsya Ltd. The LDPE-VEMAC film was prepared according to the method reported previously [6].

Fig. 1. Schematic illustration for the fabrication of durable hydrophilic surface.

A LDPE film (10 mm × 30 mm) was soaked in cyclohexanone solution containing 2% VEMA and 5% p-xylene for 6 h at 60 °C and dried in vacuo overnight. The treated LDPE film was subjected to Ar plasma-irradiation to immobilize VEMA onto the LDPE surface layer. The plasma state was generated by radio frequency discharge of inductive coupling with a five loop antenna at 13.56 MHz and a 20 W power supply. The flow volume (50 ml/min) and pressure (0.5 Torr) of argon gas were controlled by changing the evacuating speed. The sample film was placed on a glass-tripod in a reaction chamber to ensure homogeneous exposure to plasma gas. After plasma-irradiation, the hydrolysis of maleic anhydride linkage in VEMA was conducted to obtain LDPE-VEMAC film.

2.2. Procedure of immobilization of Pd nano particles on the LDPE-VEMAC film

Figure 2 shows the schematic representation of the immobilization of Pd nano particles onto the polymer support. The LDPE-VEMAC film was soaked in a mixture of water (5 mL) and 0.25 mol/L 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) solution (1 mL) at 30 °C for 2 h. After adding 0.25 mol/L hexamethylenediamine (HMDA) solution (1 mL), the film was kept at 30 °C for 20 h. After then the film was washed with water and dried in vacuo to obtain LDPE-HMDA film.

VEMA (100 mg) was dissolved into dry THF (40 ml). The LDPE-HMDA film was soaked into a VEMA solution (20 mL) and kept at 37 °C for 12 h. The film was washed with THF and dried in vacuo.

Fig. 2. Schematic representation of immobilization of Pd nano particles.

This film was immersed into 0.1 mol/L NaOH aqueous solution (200 mL) for 10 min, and then 1 mol/l HCl solution (100 mL) for 10 min. The film was thoroughly washed with water and dried in vacuo to obtain the film introducing VEMAC, LDPE-HMDA-VEMAC film.

The LDPE-HMDA-VEMAC film was soaked into 0.25 mol/L EDC solution (5 mL) at 30 °C for 2 h. To this solution was added 0.25 mol/L HMDA solution (5 mL). This reaction mixture was kept at 30 °C for 24 h. The film was washed with water and dried in vacuo to obtain the film introduced HMDA, LDPE-HMDA-VEMAC-HMDA film.

The Pd nano particle dispersion (10 mM, diameter 2 ~7 nm) was purchased from Wako Pure Chemical Industries, Ltd. The LDPE- HMDA-VEMAC-HMDA films (3 films) were soaked into 5 mL of 10
mM or 1 mM Pd nano particle dispersion to obtain LDPE films immobilizing Pd nano particles (LDPE-Pd(92) and LDPE-Pd(28)). The films were kept at room temperature for 24 h. Absorbance of Pd nano particle dispersion at 550 nm before and after reaction was measured to estimate the amount of immobilized Pd nano particles.

2.3. General procedure for the hydrogenation
Substrate (1 μmol or 10 μmol) and three or six films of LDPE-Pd(92) or LDPE-Pd(28) was added to MeOH (10 mL). This mixture was shaken with shaker under an H2 atmosphere (balloon) at 0, 30 or 50 ºC. After a specific time, the films were taken out, and the solution was concentrated in vacuo to give the corresponding spectrometricaly-pure reduced product. 1H NMR spectra measurement was performed to confirm the reduced product in comparison with the authentic sample. UV spectra were also measured to determine the yield of the reduced product.

3. Results and discussion
3.1. Immobilization of Pd nano particles
Table 1 shows the density of Pd nano particles on LDPE-HMDA-VEMAC-HMDA films which were prepared with two kinds of concentration of Pd nano particle dispersion. The films possessing 92.1 and 27.5 nmol/cm² of Pd were termed as LDPE-Pd (92) and LDPE-Pd (28), respectively.

| Film       | Density of Pd (nmol / cm²) |
|------------|-----------------------------|
| LDPE-Pd (92) | 92.1                       |
| LDPE-Pd (28) | 27.5                       |

3.2. Hydrogenation of stilbene and 4-nitroaniline with LDPE-Pd film
To confirm the hydrogenation activity of LDPE-Pd film, the hydrogenation of stilbene and 4-nitroaniline was carried out in methanol. The results are shown in Table 2.
Although stilbene was not hydrogenated with LDPE-Pd (92) film at 30 ºC for 24 h within a detectable extent, the reaction readily proceeded at 50 ºC to give dibenzyl in excellent yield (Table 2, entries 1 and 2). In the case of 4-nitroaniline with LDPE-Pd (92) at 30 ºC, 4-nitroaniline was completely consumed within 24 h, but p-phenylenediamine was not obtained to give decomposed mixtures containing hydrogenated phenyl groups (Table 2, entry 3). It was assumed that hydrogenation activity of LDPE-Pd (92) might be strong for p-phenylenediamine in this experimental condition. Therefore, we conducted this reaction at 0 ºC (Table 2, entry 4). In this condition, the reaction fairly proceeded not to give a decomposed compound.

It is known that amino groups express a catalyst-poisoning effect for Pd. In the present method Pd

| Entry | Substrate | Catalyst | Temp (ºC) | Time (h) | Product | Yield (%) |
|-------|-----------|----------|-----------|----------|---------|-----------|
| 1     | Ph−Ph     | LDPE-Pd (92) | 30        | 24       | Ph−Ph   | 0         |
| 2     | Ph−Ph     | LDPE-Pd (28) | 50        | 5        | Ph−Ph   | 99        |
| 3     | Ph−Ph     | LDPE-Pd (92) | 30        | 24       | Ph−Ph   | 0 a)     |
| 4     | Ph−Ph     | LDPE-Pd (28) | 30        | 12       | Ph−Ph   | 40        |
| 5     | Ph−Ph     | LDPE-Pd (28) | 30        | 24       | Ph−Ph   | 63        |
| 6     | Ph−Ph     | LDPE-Pd (92) | 50        | 4        | Ph−Ph   | 98        |

*a) Decomposed mixture was obtained.
nano particles bind via amino groups on LDPE-HMDA-VEMAC-HMDA film. It was considered that more free amino groups could be remained in LDPE-Pd film in the case of the lower density of Pd nano particles. Therefore, it was assumed that Pd in LDPE-Pd (28) could interact with more amino groups than that in LDPE-Pd (92), and that hydrogenation activity of LDPE-Pd (28) might be lower than that LDPE-Pd (92) due to the catalyst-poisoning effect of amino groups. In the case of 4-nitroaniline with LDPE-Pd(28) at 30 ºC, the yield was 63%, and substrate and a trace of decomposed mixtures were observed by 1H NMR. As shown in entry 6 in Table 2, p-phenylenediamine was produced in excellent yield with LDPE-Pd (28) at 50 ºC in 4 h.

4. Conclusion
The conclusions drawn from the present study can be summarized as follows.

We synthesized the polymer film immobilizing Pd nano particles by the use of a durable hydrophilic surface fabricated by the plasma-assisted method. Two kinds of film possessing different Pd nano particle density were prepared, LDPE-Pd (92) and LDPE-Pd (28). Stilbene and 4-nitroaniline were readily hydrogenated with LDPE-Pd film, indicating that the temperature and density of Pd on film might be very important for chemoselectivity.

We are now actively elaborating the hydrogenation of various compounds to clarify the chemoselectivity of LDPE-Pd film.

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