

# Imidazolium Hexafluorophosphate의 양이온이 HFP 수소화 반응용 Pd/C 촉매 제조에 미치는 영향

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## Influence of the Cation Parts of Imidazolium Hexafluorophosphate on Synthesis of Pd/C Particles as a HFP Hydrogenation Catalyst

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다양한 양이온을 가지는 imidazolium hexafluorophosphate를 이용하여 탄소담지 팔라듐 촉매를 제조하여 이를 hexafluoropropylene 수소화 반응에 사용하였다. 팔라듐의 입자형태는 사용된 이온성액체의 양이온에 영향을 받는 것이 관찰되었다. 이온성액체와 팔라듐 입자 사이의 입체적 안정화 영향으로 인하여 양이온 부분의 알킬 길이가 증가할수록 팔라듐입자는 구형에서 원통형으로 변하였다. 500 °C에서 소성한 촉매 모두 동일한 결정구조를 형성하였다. 일정한 반응조건에서 양이온에 hexyl기를 가진 이온성액체로 합성한 촉매가 가장우수한 반응성을 보였다.

Palladium on carbon catalysts for hexafluoropropylene hydrogenation were prepared using imidazolium hexafluorophosphate with various cation parts. The morphology of palladium was relatively affected by the cation parts of the ionic liquid. With increasing alkyl chains of the ionic liquid cation, the shape of palladium particle changed from spherical to cylindrical due to the effect of steric stabilization. After calcination at 500 °C, all catalysts possessed the comparable crystal structure. Under the identical reaction conditions, the catalyst prepared using the ionic liquid with hexyl chain in cation parts showed the most effective reactivity.

**Keywords:** Imidazolium Hexafluorophosphate, Hydrogenation, Pd/C particles

### 1. Introduction

Palladium (Pd) plays crucial roles in many applications such as hydrogen storage, sensing and catalyst[1-4]. Especially, Pd is most interesting for its significant ability to absorb hydrogen, up to 900 times its own volume of hydrogen at atmospheric pressure and room temperature. So, Pd can serve as a desirable catalyst for hydrogenation and dehydrogenation reactions. In the reaction, the shape of Pd particles is significant factor to control its activity. For instance, the performance of catalysts could be tailored by controlling Pd shape[5-7]. Thus, the synthesis of Pd with different morphology over support ma-

terial has been a challenging task, like other noble metals.

Recently, ionic liquids have been focused in many research areas. However, ionic liquids has little used in inorganic synthesis has. Ionic liquids, exceptional type of solvent consisting only of ions, can act as templates and precursors to inorganic materials, as well as solvents. They have numerous advantages, for example negligible vapor pressures, wide liquid ranges, good thermal stability, tunable solubility for both organic and inorganic molecules, and much synthetic flexibility. Especially, the physical and chemical properties of ionic liquids can be specifically varied over a wide range by the selection of proper cations and anions[8,9].

At present, hydrofluorocarbons (HFC), mostly 2,3,3,3-tetrafluoro-1-propene (HFO-1234yf) are candidate as a useful refrigerant in many processes. HFOs are much safer than chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) causing the ozone layer depletion and global warming. For HFO-1234yf production, hexafluoropropylene (HFP) hydrogenation is one of major processes[10]. In our previous

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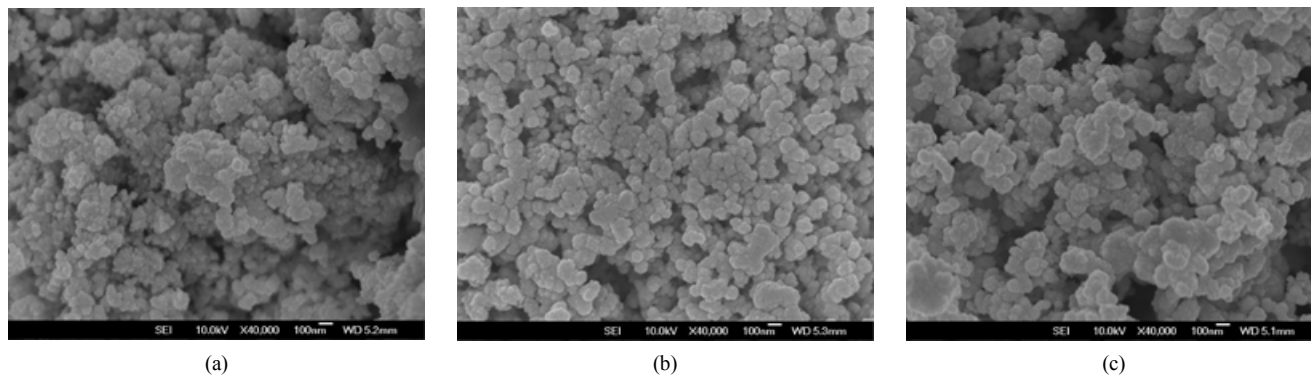


Figure 1. SEM images of Pd particles prepared with (a) [Bmim][PF<sub>6</sub>], (b) [Hmim][PF<sub>6</sub>] and (c) [Omim][PF<sub>6</sub>].

Table 1. List of Ionic Liquids Used in This Study

symbol	full name	purity (%)
[Bmim][PF <sub>6</sub> ]	1-Buthyl-3-methylimidazolium hexafluorophosphate	97
[Hmim][PF <sub>6</sub> ]	1-Hexyl-3-methylimidazolium hexafluorophosphate	97
[Omim][PF <sub>6</sub> ]	1-Octyl-3-methylimidazolium hexafluorophosphate	97

work[11,12], Pd particles were formed variously with the type of ionic liquids during synthesis. Especially, Pd on carbon powders (Pd/C) prepared using ionic liquid with anion parts of hexafluorophosphate ([PF<sub>6</sub>]) showed desirable catalytic activity due to its favorable Pd shape. In this work, Pd/C particles prepared with imidazolium hexafluorophosphate with various cation parts to investigate the effect on Pd synthesis. The prepared materials were examined in HFP hydrogenation to investigate a high performance catalyst.

## 2. Experimental

For the preparation of palladium particle, Na<sub>2</sub>PdCl<sub>4</sub> (99.8%, Sigma-aldrich) was dissolved in the distilled water, and then added ionic liquids (C-try, Korea) listed in Table 1, respectively. After the solution was stirred for 10 min, NaBH<sub>4</sub> (99%, Sigma-aldrich) was added to obtain palladium particles. Pd/C was prepared by wet impregnation method. Na<sub>2</sub>PdCl<sub>4</sub> was mixed with distilled water. After then ionic liquid was added with stirring. Reduction solution was prepared by NaBH<sub>4</sub> and distilled water. Finally, carbon powder (99.95%, Sigma-aldrich) was added in the mixture, and then reduction solution was added by drop-wise. The detail procedure can be found elsewhere[11,12]. The obtained powder was washed with methanol for 2 h. Pd/C catalyst was recovered by filtration, and then calcined for 2 h.

XRD patterns of Pd/C particles were recorded by an X-ray diffractometer (Shimadzu XRD-6000) operated at 40 kV and 30 mA, using

Cu Ka ( $\lambda = 0.15418$  nm) radiation to determine the crystal structure. The structural properties of the samples were measured using a N<sub>2</sub> sorption method (BELSORP-MINI II, BEL Co.). The images of samples were confirmed using scanning electron microscopy (SEM, JSM-6700F, JEOL Co.) and transmission electron microscopy (TEM, CM-30, Philips Co.). The properties of Pd on Pd/C particles were measured by CO chemisorptions (BELCAT-B, BEL Co.) at room temperature using a pulse flow technique.

Catalytic reaction was performed in a fixed-bed reactor. The catalyst (typically 0.10 g) was loaded in a 1/8-in. inner diameter stainless-steel vertical tube containing a thermocouple. For the reaction, the catalyst was reduced in a 5% H<sub>2</sub> gas (20 cc/min) at 200 °C for 2 h. After the reduction, the reactant gas mixture composed of H<sub>2</sub> (25 cc/min) and HFP (40 cc/min) was introduced into the reactor at GHSV<sub>HFP</sub> of 48,000 ml/g<sub>cat</sub>-h. The products were analyzed using an on-line gas chromatograph (Agilent 6890) with FID detector. The GC column used for separation was a HP-5 capillary column (30 m × 0.32 mm).

## 3. Results and Discussion

In our previous work[12], the shape of Pd particle was significantly affected by the type of anion parts of ionic liquids. Especially, the ionic liquids with hexafluorophosphate in an anion parts were effective to form a relatively small size and regular shape of Pd particle. For the reason, Pd particles were prepared by three ionic liquids with different cation parts to investigate the effect of ionic liquids. SEM images of Pd particles prepared by three ionic liquids are shown in Figure 1. The size of aggregation of Pd particles was slightly increased with the length of cation parts of ionic liquids. The crystal structure of Pd particle was determined by XRD analysis. The patterns of the samples are shown in Figure 2. Four diffraction peaks at 40.1°, 46.6°, 68.2° and 82.1° of Bragg reflection were observed over all samples. They are indexed to the (111), (200), (220) and (311) planes of the pure fcc crystal structure. This means all sample possess pure palladium crystal structure.

The shapes of Pd particles were observed by TEM analysis as illustrated in Figure 3. The cation parts of ionic liquids gave an effect on the formation of Pd particle. The sample prepared with [Bmim][PF<sub>6</sub>]

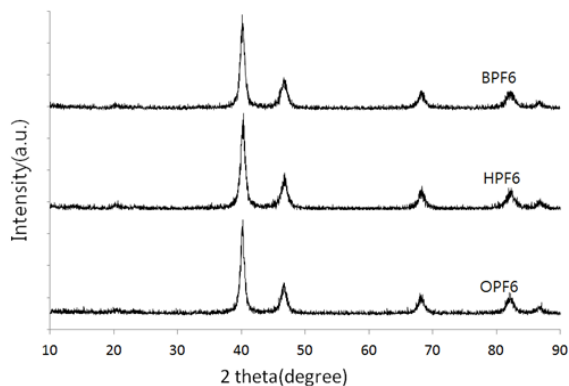


Figure 2. XRD patterns of Pd particles prepared with [Bmim][PF<sub>6</sub>], [Hmim][PF<sub>6</sub>] and [Omim][PF<sub>6</sub>].

Table 2. Properties of Pd Particles Prepared with Ionic Liquids with Various Cation Parts

sample	Surface area (m <sup>2</sup> /g)	Pore volume (cc/g)	Pore diameter (nm)
[Bmim][PF <sub>6</sub> ]	23	5.3	44.4
[Hmim][PF <sub>6</sub> ]	23	5.4	42.6
[Omim][PF <sub>6</sub> ]	14	8.8	101.3

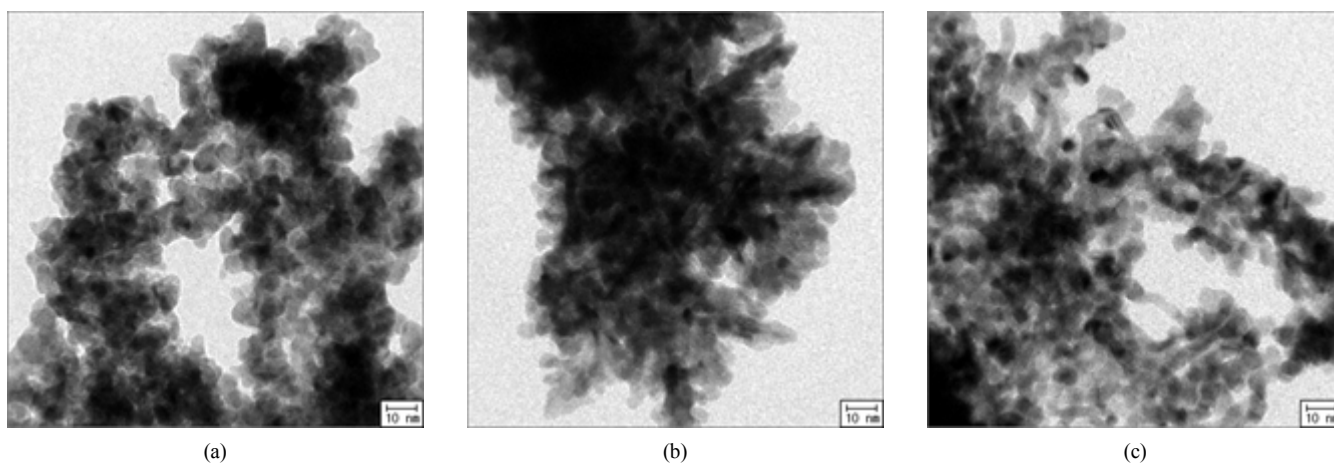


Figure 3. TEM images of Pd particles prepared with (a) [Bmim][PF<sub>6</sub>], (b) [Hmim][PF<sub>6</sub>] and (c) [Omim][PF<sub>6</sub>].

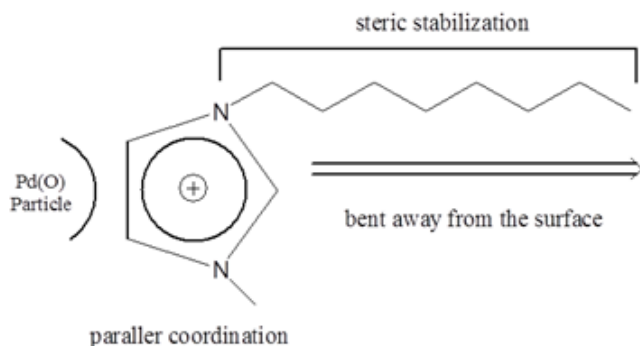


Figure 4. Scheme of imidazolium cation coordination and stabilization mode.

shows a hierarchical porous ball like structure with relatively small and uniform size. With increasing alkyl chain length of cation parts of ionic liquids, the shape of Pd particle was changed to rod like structure with relatively irregular aggregation. The structural properties of Pd particles are presented in Table 2. Both samples prepared by [Bmim][PF<sub>6</sub>] and [Hmim][PF<sub>6</sub>] possessed comparable properties. However, the properties of the sample prepared by [Omim][PF<sub>6</sub>] were changed; the surface area decreasing, but pore volume and pore diameter increasing. Thus, the

cation part of ionic liquids played a role in the formation of Pd particle. This result suggests that the imidazolium ring interacted with the Pd particle surface via a parallel coordination mode as illustrated in Figure 4. Moreover, the cation parts can be responsible for the steric stabilization component because of the arrangement of the tail attached to the imidazolium ring. Electrostatic stabilization occurs by the adsorption of ions on the electrophilic metal surface. This creates an electrical double layer, which results in a Coulombic repulsion force between individual particles. Steric stabilization is achieved by surrounding the metal center by layers of material that are sterically bulky, such as polymers or surfactant. These large adsorbates provide a steric barrier which prevents close contact of the metal particle centers[13].

After impregnation of Pd on carbon power under identical condition without using various ionic liquids, the Pd/C particles were obtained as a catalyst for HFP hydrogenation. The structural properties of Pd/C particles are presented in Table 3. The particle with the highest surface area and the lowest pore volume and pore diameter was obtained using [Bmim][PF<sub>6</sub>]. With increasing the alkyl chain length, the trend was shifted in reverse way. Thus the effect of an ionic liquid on determining the properties of Pd/C particles was significant as well. The XRD patterns of all samples are shown in Figure 5. All samples possessed

**Table 3. Properties of Pd/C Particles Prepared with Ionic Liquids with Various Cation Parts**

sample	Surface area (m <sup>2</sup> /g)	Pore volume (cc/g)	Pore diameter (nm)
[Bmim][PF <sub>6</sub> ]	75	0.27	14
[Hmim][PF <sub>6</sub> ]	51	0.45	35
[Omim][PF <sub>6</sub> ]	49	0.77	64

**Table 4. Properties of Pd Particles on Carbon Supports Prepared with Ionic Liquids with Various Cation Parts**

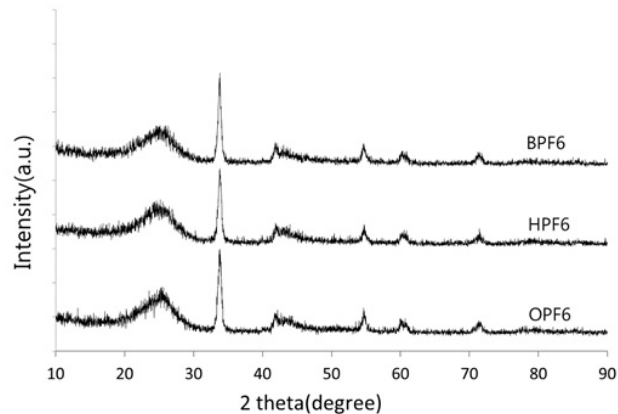
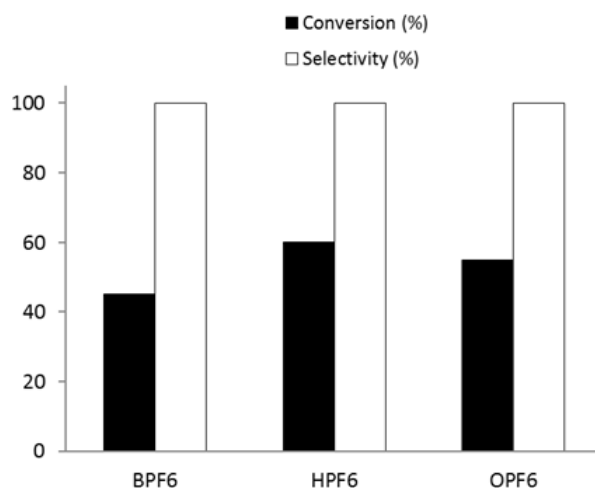
sample	Metal dispersion (%)	Metal surface area (m <sup>2</sup> /g)	Metal diameter (nm)
[Bmim][PF <sub>6</sub> ]	1.6	7.2	69.5
[Hmim][PF <sub>6</sub> ]	0.7	3.0	164.0
[Omim][PF <sub>6</sub> ]	0.5	2.3	219.9

a comparable crystal structure. In addition to four diffraction peaks indexed to the pure palladium crystal structure, both diffractions (at  $2\theta = 25^\circ$  and  $44^\circ$ ) of carbon black were observed as well.

The hydrogenation of 1,2,3,4,5,6-HFP was carried out at a temperature of 120 °C and atmospheric pressure. The main product was 1,1,2,3,3,3-hexafluoropropylene and small amount of hexafluoropropylene isomers were detected without any impurity. The catalytic activity of Pd/C particles prepared using various cation parts of ionic liquids was shown in Figure 6. The catalytic activity of Pd/C particle prepared using [Hmim][PF<sub>6</sub>] outperformed to the others. The catalyst prepared with [Bmim][PF<sub>6</sub>] showed the lowest catalytic performance. The selectivity of main product was comparable over all samples. The properties of palladium on carbon particle were measured by hydrogen chemisorption as illustrated in Table 4. Interestingly, smaller size of palladium was formed using less alkyl chain of ionic liquid. Interestingly, Pd/C particle with medium metal size showed the highest catalytic performance in this reaction. This means that the size of metal as an active site is not crucial to determine the catalytic activity. It might be the shape of metal on the support is more important factor in this reaction.

#### 4. Conclusions

Controlling a shape and size of palladium on carbon support was accomplished using imidazolium hexafluorophosphate, a water immiscible room temperature ionic liquid, as an effective solvent. It was observed that the morphology of palladium particle on carbon was affected with cation parts of the ionic liquids. Especially, the desirable

**Figure 5. XRD patterns of Pd/C particles prepared with [Bmim][PF<sub>6</sub>], [Hmim][PF<sub>6</sub>] and [Omim][PF<sub>6</sub>].****Figure 6. Catalytic activity of Pd/C particles prepared with [Bmim][PF<sub>6</sub>], [Hmim][PF<sub>6</sub>] and [Omim][PF<sub>6</sub>].**

shape of active site was showed higher catalytic activity for a HFP hydrogenation. Thus, this synthesis method could be used to impregnation of novel metals on several carbon based support materials. With advance investigations, this methodology can be used in numerous applications of nanotechnology.

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