

# Synthesis of Pd particles with various shapes by ionic liquids for HFP hydrogenation catalyst

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**Abstract** Palladium particles were simply synthesized using various ionic liquids. The morphology of the particles was significantly affected by the anion parts of the ionic liquids. Among the ionic liquids, hexafluorophosphate as an anion part was more effective in forming the palladium particles with relatively small and narrow size distribution. However, irregularly shaped palladium particles were synthesized without ionic liquid assistance. For a hexafluoropropylene hydrogenation to produce hydrofluorocarbons, palladium was impregnated on a carbon powder as a catalyst. During the preparation of the catalyst, ionic liquids were added to control the shape of the palladium on the support. After calcinations at 500 °C, all catalysts possessed the comparable crystal structure. Under identical reaction conditions, the catalyst prepared using 1-hexyl-3-methylimidazolium hexafluorophosphate was the most effective in this reaction. Hence, catalytic activity was mainly determined by the size of the palladium particles.

**Keywords** Palladium particles · Ionic liquid · Shape control · HFP hydrogenation

## Introduction

Palladium plays essential roles in hydrogen storage, sensing, and catalysts [1–4]. Especially, the size and shape of the Pd particles are crucial parameters in

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controlling its performance in these applications. In some cases, shape control can allow one to adjust its properties with a better versatility. For example, the performance of catalysts could be tailored by controlling the shape [5–8]. Thus, the synthesis of Pd with various shapes has been a demanding task, like other noble metals.

Ionic liquids have been extensively studied in solvent extraction and organic catalysis, but their use in inorganic synthesis has only just begun. Ionic liquids, an exceptional type of solvent consisting of virtually only ions, can act as templates and precursors to inorganic materials, as well as solvents. They present many advantages, such as negligible vapor pressures, wide liquid ranges, good thermal stability, tunable solubility for both organic and inorganic molecules, and great synthetic flexibility [9, 10].

Hydrofluorocabons (HFC), particularly 2,3,3,3-tetrafluoro-1-propene (HFO 1234yf), are useful refrigerants in many processes. Unlike CFCs and HCFCs, which are potentially hazardous to the ozone layer and global climate, HFOs is safe to the issues. Hexafluoropropylene (HFP) hydrogenation is one of the key steps to produce HFO 1234yf [11]. In this reaction, Pd dispersed on carbon support is usually used as a desirable catalyst. In this work, ionic liquids were employed to control Pd morphology during the impregnation of the Pd on carbon power. The prepared materials were tested in HFP hydrogenation to obtain a high performance catalyst.

## Materials and methods

### Particle preparation

For the preparation of palladium particles,  $\text{Na}_2\text{PdCl}_4$  (99.8 %; Sigma-Aldrich) was dissolved in distilled water and then an ionic liquid was added. Ionic liquids, 1-hexyl-3-methylimidazolium hexafluorophosphate ([Hmim][PF<sub>6</sub>]), 1-hexyl-3-methylimidazolium tetrafluoroborate ([Hmim][BF<sub>4</sub>]), and 1-hexyl-3-methylimidazolium trifluoromethanesulfonate ([Hmim][CF<sub>3</sub>SO<sub>3</sub>]) were purchased from C-Try. After the mixed solution was stirred for 10 min,  $\text{NaBH}_4$  (99 %; Sigma-Aldrich) was added to obtain the palladium particles. The detailed procedure can be found elsewhere [12]. Pd on carbon powder (Pd/C) was prepared by the wet impregnation method, with 0.15 g  $\text{Na}_2\text{PdCl}_4$  mixed with 10.5 mL distilled water. Then, the ionic liquid was added with stirring. A reduction solution was prepared by 0.02 g of  $\text{NaBH}_4$  and 4.5 mL distilled water. Finally, 1.5 g of carbon powder (99.95 %; Sigma-Aldrich) was added in the mixture and finally 1 mL reduction solution was added dropwise. This solution was kept at 100 °C until dried to powder. The powder was washed with methanol for 2 h. The Pd/C catalyst was obtained by filtration and then calcined at 500 °C for 2 h.

### Characterization

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

CuK $\alpha$  ( $\lambda = 0.15418$  nm) radiation to determine the crystal structure. The surface area of the samples was measured using the N<sub>2</sub> sorption method with a BELSORP-MINI II instrument (BEL). The sample images were confirmed using TEM (Philips CM-30; Philips). The Pd particle size on the Pd/C particles was measured by CO chemisorptions (BELCAT-B; BEL) at room temperature using a pulse flow technique.

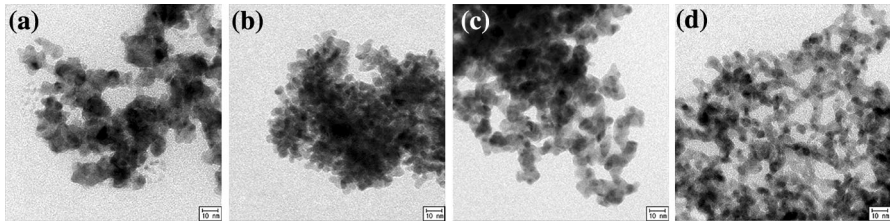
### Hydrogenation reaction

Catalytic reaction was performed in a fixed-bed reactor with 3/8 in. inner diameter. For the reaction, the catalysts were reduced in a 5 % H<sub>2</sub> gas at 200 °C for 2 h. After the reduction, the reactant gas mixture composed of H<sub>2</sub> and HFP (H<sub>2</sub>/HFP = 0.6) was introduced into the reactor at GHSV of 77,000 mL/g<sub>cat</sub>-h. The products were analyzed using an on-line gas chromatograph (Agilent 6890) with a FID detector.

## Results and discussion

In our previous work [12], the shape of Pd particles was affected by the length of the alky-group in the ionic liquid. Especially, the ionic liquids with a hexyl chain in the cation part were effective in forming the relatively small size and regular shape of the Pd particles. This result was attributed to the different steric stabilization effect of the alkyl chains in ionic liquids [13]. However, the effect of the cation part on the formation of Pd particles was not sufficient to control catalytic activity as a catalyst. For this reason, Pd particles were prepared by three ionic liquids with different anion parts to investigate the effect of ionic liquids. Moreover, the particles prepared without ionic liquid, 'pure', was used as the control sample for comparison with the other samples.

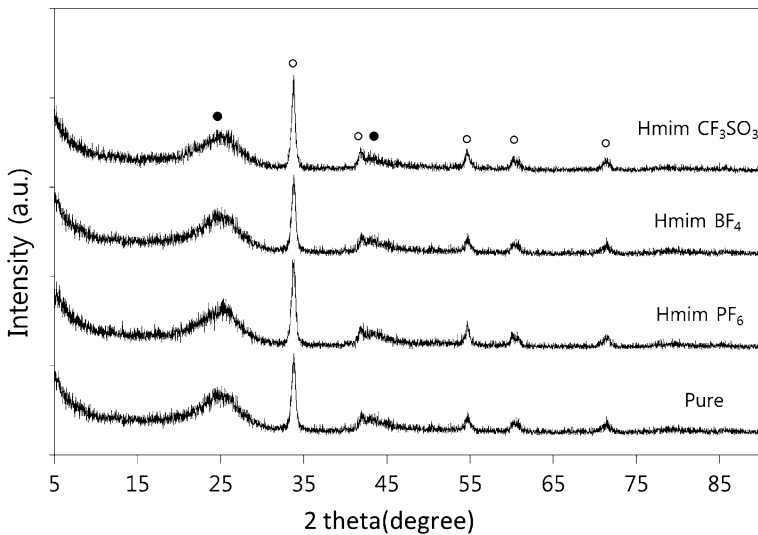
TEM images of Pd particles are shown in Fig. 1. The shapes of the particles were significantly affected by the anion parts of the ionic liquids. The Pd particles prepared without ionic liquid were formed irregularly as shown in Fig. 1a. This is attributed to random aggregation of the Pd particles during the synthesis. In the case of ionic liquids, the shape of the Pd particles was somewhat controlled by their anion parts. Among the ionic liquids, [Hmim][BF<sub>4</sub>] gave a trivial effect as shown in Fig. 1c. Indeed, the shape of Pd particles prepared with [Hmim][BF<sub>4</sub>] was relatively comparable to the 'pure' sample. However, the other ionic liquids showed considerable effects on the formation of Pd particles. The shape of sample prepared with [Hmim][PF<sub>6</sub>] is shown in the TEM pictures in Fig. 1b. The picture shows a hierarchical porous ball-like structure with relatively small and uniform sizes. Moreover, the particles prepared using [Hmim][CF<sub>3</sub>SO<sub>3</sub>] were shaped like the branched chain networks as shown in Fig. 1d. This is attributed to the interactions of the ionic liquid with the metal surface demonstrating the formation of an ionic liquid protective layer surrounding the Pd particles. Indeed, the extended molecular lengths of the ionic liquids were affected by their anion parts [14]. The surface area of the Pd particles after being calcined at 500 °C varied with the ionic liquids used in synthesis as illustrated in Table 1. The highest surface area, 23.6 m<sup>2</sup>/g, was



**Fig. 1** TEM images of Pd particles prepared using various ionic liquids: **a** pure, **b** [Hmim][PF<sub>6</sub>], **c** [Hmim][BF<sub>4</sub>], **d** [Hmim][CF<sub>3</sub>SO<sub>3</sub>]

**Table 1** Properties of samples prepared with various ionic liquids

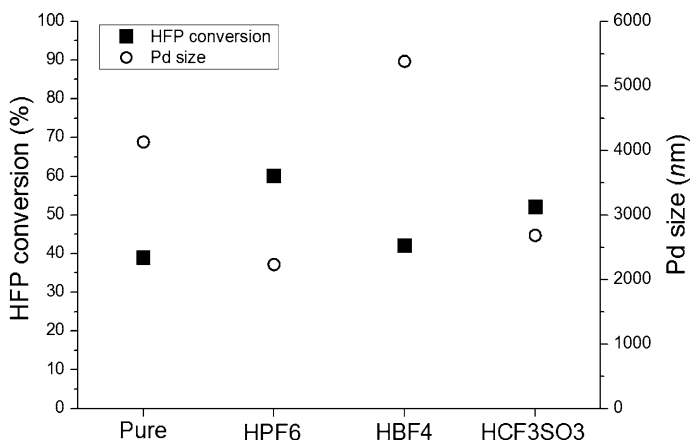
Sample	Pd particle surface area (m <sup>2</sup> /g)	Pd/C surface area (m <sup>2</sup> /g)	Pd/C pore volume (cc/g)
Pure	9.0	69.2	0.456
[Hmim][PF <sub>6</sub> ]	23.6	54.2	0.357
[Hmim][BF <sub>4</sub> ]	10.2	70.5	0.416
[Hmim][CF <sub>3</sub> SO <sub>3</sub> ]	11.8	66.9	0.486



**Fig. 2** XRD patterns of Pd/C particles prepared using various ionic liquids. The marks indicate the structure of PdO (circle) and carbon black (solid)

obtained for the [Hmim][PF<sub>6</sub>] sample, while the [Hmim][BF<sub>4</sub>] sample showed the lowest surface area, 9.0 m<sup>2</sup>/g. This is in a good agreement with TEM results.

The XRD patterns (not shown) of all the Pd particles revealed four diffraction peaks indexed to the (111), (200), (220) and (311) planes of the pure Pd fcc crystal



**Fig. 3** Correlation of the Pd size on Pd/C particles to HFP conversion

structure, respectively. The XRD patterns of the Pd/C samples are shown in Fig. 2. The reflections of the metallic fcc-phase disappeared, but the peaks indexed to the (002)(101), (110), (112) and (103)(200) planes assigned to tetragonal PdO phase were clearly exposed. Strong diffractions of carbon black were also observed. Interestingly, the XRD patterns of all the samples were closely comparable. This means that the differences of the crystal structure between the samples were not significant.

The structural properties of the Pd/C particles are presented in Table 1. The surface area and pore volume of the Pd/C particles were comparable except for the Pd/C particle prepared with [Hmim][PF<sub>6</sub>]. The sample possessed a slightly lower surface area and pore volume than the others. Interestingly, the lowest surface area of the Pd/C particles was formed by [Hmim][PF<sub>6</sub>] assisting the highest surface area of the Pd particles produced.

The hydrogenation of 1,2,3,4,5,6-HFP over the Pd/C particles was carried out at a temperature of 120 °C and under a constant H<sub>2</sub> pressure of 0.1 MPa. The main reaction product was 1,1,2,3,3,3-hexafluoropropylene. Small amounts of hexafluoropropylene isomers were detected, but the formation of other impurities was hardly observed. Correlation between the catalytic activity and Pd particle size on Pd/C particles is shown in Fig. 3. Among the catalysts, Pd/C particles prepared with [Hmim][PF<sub>6</sub>] yielded the highest HFP conversion, but Pd/C particles prepared without ionic liquid showed the lowest. It was clearly observed that the smaller metal size on the catalyst gave a desirable effect on the hydrogenation activity. This means that the size of the Pd particles might be a crucial factor to determine the catalytic performance under identical conditions.

## Conclusion

Controlling a shape of materials can encourage the development of products with improved properties and functionality for several applications. In this study,

palladium on carbon was synthesized by a simple and easy method to scale-up using ionic liquids. Ionic liquids played a crucial role in determining the morphology of the palladium particles. Especially, the size of the palladium gave a direct effect on determining the catalytic performance. In HFP hydrogenation, the catalyst prepared with [Hmim][PF<sub>6</sub>] outperformed the others.

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