


팔리듐 담지 다공성 폴리우레아를 불균일 촉매로 활용한 Suzuki-Miyaura 커플링 반응

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Palladium Supported Porous Polyurea Frameworks as an Efficient Heterogeneous Catalyst for Suzuki-Miyaura Cross-coupling Reaction

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초록: 다공성 고분자(porous organic polymer, POPs)는 높은 표면적을 가지는 무정형의 고분자이다. 본 연구에서는 우레아 축합반응으로 UPOP라는 다공성 고분자를 합성하였다. UPOP는 Brunauer-Emmett-Teller(BET) 분석을 통해 다공성을 확인하였고, 불균일 촉매 활용성을 보기 위하여 팔리듐을 담지하여 Pd@UPOP를 합성하였다. Pd@UPOP는 XPS 분석을 통해 Pd 담지를 확인하였고, Suzuki-Miyaura 커플링 반응을 이용하여 촉매활성을 측정하였다. Pd@UPOP의 촉매활성은 물과 ethanol이 3:1이고 K₂CO₃를 사용하였을 때 가장 높았다. 특히 이 조건에서 Pd@UPOP를 촉매로 사용하여 공기 중에서 반응시켰을 때 Pd 함량은 0.1 mol%였음에도 불구하고 99% 이상의 수율을 보였다. 또한 5번 재사용하였을 때도 90%의 수율을 유지하였다.

Abstract: Porous organic polymers (POPs) are composed of amorphously linked bonds with high surface areas. Urea based porous organic polymer (UPOP) was synthesized by urea condensation reaction. Porous nature of UPOP was identified by Brunauer-Emmett-Teller (BET) analysis. To evaluate the possibility as heterogeneous catalysts, Pd was loaded onto UPOP, namely Pd@UPOP. XPS analysis and element mapping data confirmed that Pd was supported on Pd@UPOP, then Suzuki-Miyaura coupling reaction was performed with various aryl bromides. The optimized conditions for the catalytic activity of Pd@UPOP are using mixture of (H₂O:EtOH 3:1) (v/v) as a solvent and K₂CO₃ as a base. In this condition, reactions reached to 99% yields with Pd only 0.1 mol% under 1 h. Also, in recycling experiments, yields were maintained above 90% during five runs.

Keywords: porous organic polymer, polyurea, Suzuki-Miyaura cross-coupling, catalyst, recycle.

Introduction

As organic chemistry has become more sophisticated, catalysts are required to have more functions for reaction rate control, reduction of activation energy of reaction, and selective reaction progress. Therefore, developing an optimized catalyst for the reaction is always an important issue. Although homogeneous catalysts are usually highly active and selective, these catalysts are hard to separate from the reaction mixture and difficult to recycle for multiple runs. In these senses, het-

erogeneous catalysts are often preferred. As prerequisites of the heterogeneous catalyst, the structure should be stable, and the transition metal should be well supported. The nitrogen-rich polymers are considered to fulfill these prerequisites under which the catalyst can be supported.¹

Porous organic polymers (POPs) are noticeable materials with special properties such as surface permanent porosity and a large surface area. In addition, POPs have been recently used in gas storage,²⁻¹⁰ sensing,^{11,12} light emitting,^{4,11,13-15} and heterogeneous catalysts¹⁶⁻²⁰ because of their ability to control pore size and tune functional groups by easy chemical reactions. Especially in recent years, significant advances have been made to use POPs as heterogeneous phase catalysts because many reactions use expensive noble metals as catalysts. When

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noble metals are used as direct catalysts, noble metals may be aggregated so reaction efficiency is lowered. In addition, depending on the reaction, a ligand that changes the state of electrons in a noble metal is required. In order to use the large surface area of POPs as catalyst supports, attempts also have been directed to prevent the aggregation of precious metals and to manipulate the structure to change the electronic state of the noble metals.^{17,18} In this regard, nitrogen-rich polymers could be good candidates since they have a high affinity for metals.

A urea group, which has been reported long ago, have many advantages since it can be formed by simple condensation reaction under the mild condition without byproduct molecules.²¹ Urea-based polymers can be synthesized with relatively inexpensive starting materials and they have high affinity with various solvents.²¹ Moreover, since the structure contains a large amount of N and O, many sites that can absorb the transition metal are expected to be useful as heterogeneous catalysts.

Suzuki-Miyaura cross-coupling reaction is one of the most important reactions for building up C-C bonds. Since the C-C construction is so useful, coupling reaction is widely in various fields. This reaction is used in agricultural chemistry, electrochemistry, pharmaceutical, natural products, and so on. Most Suzuki-Miyaura cross-coupling reactions are performed using palladium catalysts and the catalyst performance is largely dependent on the ligand of palladium. Especially, in the earlier days, the palladium loading performance of a phosphine ligand was known to be excellent, and the electronic properties of the phosphine ligand could be easily changed by controlling the functional groups, therefore it has been widely used for the Suzuki-Miyaura reaction.²²⁻²⁴ However, phosphorus ligands are less preferred due to their cost and toxicity. Recently, nitrogen-based ligands have attracted more attention. Not only nitrogen-based ligands can be synthesized with relatively economic reagents but also steric and electronic properties of nitrogen-based ligands are easily tunable by Schiff bases,²⁵⁻²⁸ hydrazones,^{29,30} amines,³¹ etc.

In this study, we prepared POP containing urea group namely, UPOP by one-step condensation polymerization of 1,4-phenylene diisocyanate with melamine, respectively. We evaluated pore structure, structure properties, thermal properties of UPOP by SEM, TEM, BET, FTIR, NMR, TGA, and XPS. The UPOP was immobilized with palladium for catalytic performance for Suzuki-Miyaura cross-coupling reaction. We optimized the reaction conditions and tested the recycling capability of the as-prepared catalysts.

Experimental

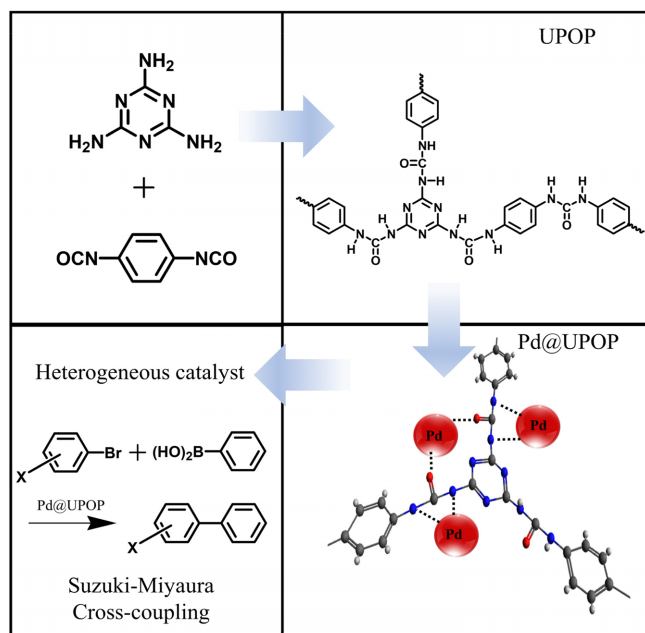
Materials. 1,4-Phenylene diisocyanate, melamine, dimethyl sulfoxide (DMSO), palladium acetate, 4-bromoanisole, 2-bromoanisole, 4-bromotoluene, 2-bromotoluene, bromobenzene, 4-bromoacetophenone, and chloroform were purchased from Sigma Aldrich Co. 2-Bromopyridine and 3-bromopyridine were purchased from Toyko Chemical Industry Co. 1-Bromo-4-nitrobenzene, 4-bromobenzonitrile, and 2-bromothiophene were purchased from Alfa Aesar. All these chemicals were used as received without further purification.

Synthesis of Urea-Based Porous Organic Polymer. UPOP was prepared by adopting a urea reaction in a 100 mL round flask. 2 mmol of melamine was melted in DMSO under Ar condition then 3 mmol of 1,4-phenylene diisocyanate was added in flask. Reaction was carried out at 150 °C with vigorous stirring under Ar condition for 24 h. After the reaction, product was filtered by centrifugation and repeatedly washed with ethanol. Product was dried in vacuo at 85 °C for 24 h, then white powder is obtained (Figure 1) The entire procedure for the preparation of Pd-supported UPOP is illustrated in Scheme 1.

Immobilization of Pd on UPOP. UPOP (292.5 mg) was added to a solution of palladium acetate (0.75 mg) in chloroform (40 mL). The mixture was dispersed using ultrasonic for 3 min. After the mixture was stirred at 70 °C for 5 h, the resultant solid was filtered and successively washed with ethanol. The residue was dried in vacuo at 80 °C for 24 h, then yellowish powder was obtained.



Figure 1. Digital photograph of as-prepared polyurea-based POP (UPOP) synthesized by condensation between melamine and 1,4-phenylene diisocyanate.



Scheme 1. Synthesis of urea-based POPs and subsequent Pd-loaded POPs for catalysts in Suzuki-Miyaura cross-coupling reaction.

Suzuki-Miyaura Cross-coupling Reaction. Pd@UPOP (0.1 mol%) was added to a mixture of aryl bromide (0.2 mmol), phenylboronic acid (0.24 mmol), and base (0.2 mmol) in solvent (4 mL). Reaction was carried out at 80 °C for 1 h under air atmosphere. After reaction, the crude product was extracted with diethyl ether and dried over anhydrous MgSO_4 and evaporated under reduced pressure. The product was purified using column chromatography. GC analysis was performed to determine the yield of reactions.

Recycle of Catalysts. Recycling experiment was carried out in presence of Pd@UPOP (0.1 mol%), 4-bromoanisole (37.4 mg, 0.2 mmol), phenylboronic acid (29.4 mg, 0.24 mmol) and K_3PO_4 (0.4 mmol) in solvent (EtOH 1 mL, H_2O 3 mL) at 80 °C for 1 h under ambient condition. After the completion of the reaction, the catalyst was separated from the reaction mixture by filtration. Then, it was directly used in the next run under the same reaction conditions.

Measurements. FTIR spectra of UPOP and Pd@UPOP were analyzed using VERTEX 80 V FTIR vacuum spectrometer. Analysis was carried out in the frequency range of 400 to 4000 cm^{-1} . ^{13}C NMR spectrum of UPOP was analyzed using DIGITAL AVANCE III 400 MHz Bruker NMR spectrometer using CDCl_3 as a solvent. Analysis was performed at 400 MHz for 128 scans. Solid NMR was performed under the same condition. Thermogravimetric analysis (TGA) was per-

formed using Q50 (TA Instruments, USA) from 40 to 900 °C at 10 °C/min under nitrogen atmosphere. Morphology was analyzed by scanning electron microscope (SEM, S-4300, Hitachi) and transmission electron microscope (TEM, JEM2100F, JEOL). Specific surface area using Brunauer-Emmett-Teller (BET) method was analyzed using BELSROP-MAX (MicrotracBEL, USA). The pore size was obtained by the non-local density functional theory (NL-DFT) method. X-ray photoelectron spectroscopy (XPS) spectra were obtained using K-Alpha model of XPS spectrometer (Thermo Scientific, USA) and elemental analysis was performed on carbon, nitrogen, oxygen, and palladium. Inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 7300DV) analysis was performed to measure the loaded amount of Pd. The yields of cross-coupling reactions were analyzed using gas chromatography (Agilent 7980A, Agilent Technologies). The analytical temperature was 150 °C and diethyl ether at a flowing rate of 6 mL/sec was used as a mobile phase.

Results and Discussion

Structural Properties. The synthetic route of UPOP is shown in Scheme 1. UPOP was characterized using FTIR as illustrated in Figure 2. The peaks observed at 3332 and 1640 cm^{-1} are N-H group and C=O stretching of urea group, respectively.³² The N=C=O peak at 2270 cm^{-1} disappeared after reaction,³² meaning that the isocyanate group reacted to become polyurea resulting in UPOP. FTIR spectra of Pd@UPOP is also displayed in Figure 2. The peaks of Pd@UPOP are same as UPOP, which indicates that the chem-

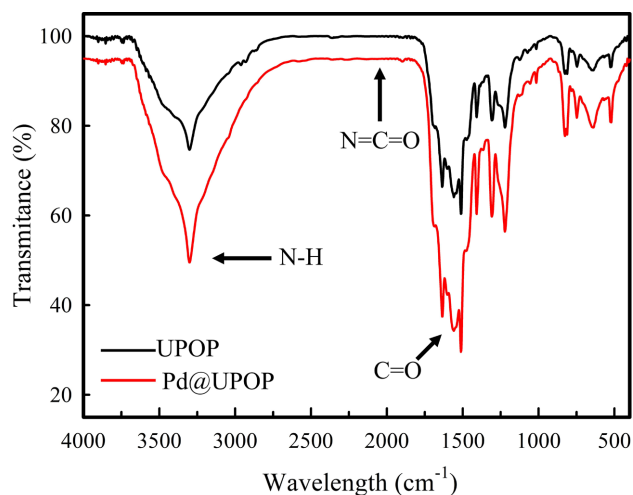


Figure 2. FTIR spectra of UPOP and Pd@UPOP catalyst.

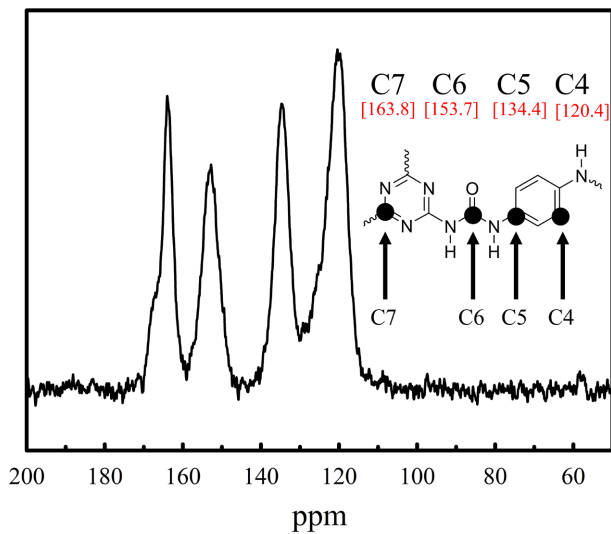


Figure 3. Solid ^{13}C NMR spectrum of as-prepared UPOP synthesized by condensation between melamine and 1,4-phenylene diisocyanate.

ical structure of UPOP remains intact after loading of palladium onto UPOP. Figure 3 shows ^{13}C NMR spectrum of UPOP where four strong peaks are witnessed. C4 and C5

peaks at 120.4 and 134.4 ppm are attributed to carbons at phenyl ring. C6 peak at 153.7 ppm originated from urea group and C7 peak at 163.8 ppm is caused by carbons at melamine. All the peaks in UPOP match with polymers with similar structure.¹¹

Surface Properties. BET analysis for P/P_0 between 0 and 1 were performed for identifying the surface area of products by N_2 adsorption-desorption at 77 K in Figure 4. The specific surface area of UPOP was measured to be $125.28 \text{ m}^2/\text{g}$. The reason UPOP has a high surface area is that UPOP has a tri-branched structure. Similar result was reported for urea-based porous polymers synthesized by 1,3,5-trisocyanate and p-phenylene diamine, in which the surface area was $91\text{--}113 \text{ m}^2/\text{g}$.²¹ The pore-size distribution of UPOP calculated using a non-local density functional theory (NL-DFT) showed a wide range of size upto several hundreds nanometers.

Morphology of UPOP and Pd@UPOP observed by SEM and TEM are depicted in Figure 5 and Figure 6. Plate-type structures are confirmed in UPOP using SEM and TEM. Elemental mapping shows that four elements (C, O, N, Pd) are homogeneously distributed in Pd@UPOP, implying that the

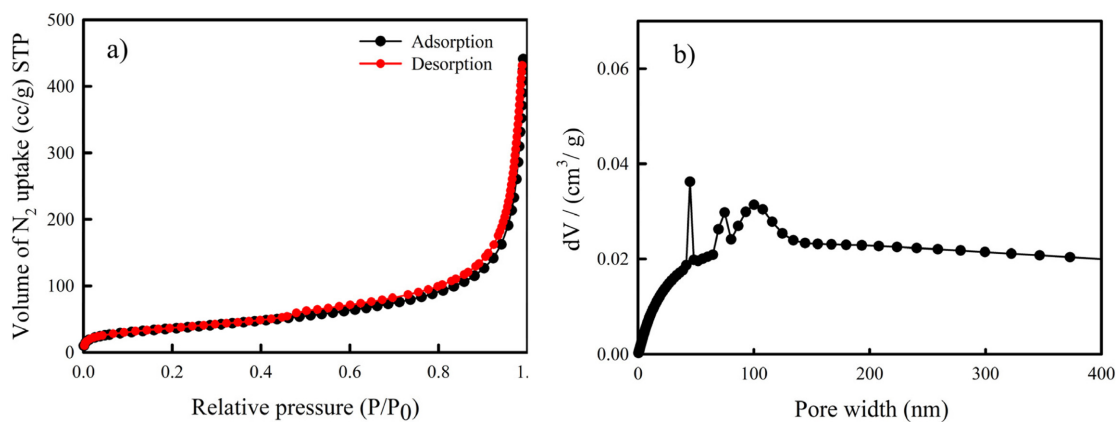


Figure 4. N_2 adsorption-desorption isotherms and pore-size distribution of UPOP at 77 K.

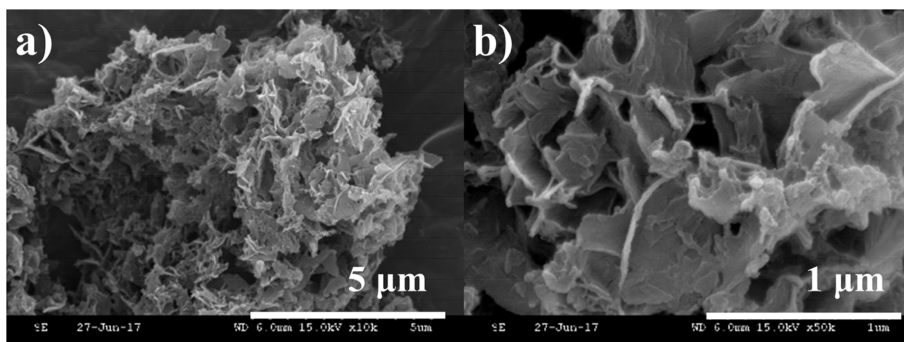


Figure 5. SEM microphotographs of UPOP at different magnifications: (a) $\times 10 \text{ K}$; (b) $\times 50 \text{ K}$.

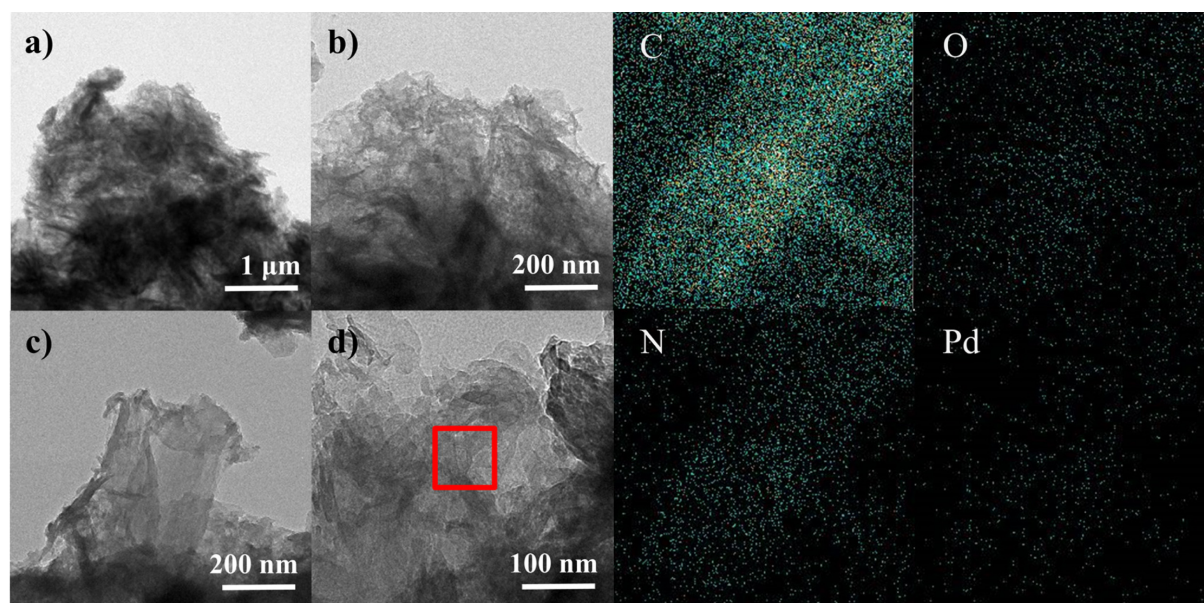


Figure 6. (left) TEM microphotographs: (a, b) UPOP; (c, d) Pd@UPOP catalyst. (right) Elemental mapping images of Pd@UPOP for C, O, N, and Pd.

catalyst is successfully prepared.

Thermal Properties. Thermal stability of UPOP and Pd@UPOP analyzed using TGA are shown in Figure 7. Structural stability at high temperature is an important issue for the scaffold because the heterocyclic system may react at high reaction temperature. We have designated the point where the structure collapses at 5% as the degradation point. Figure 7 shows that the framework degradation temperatures are 263 and 266 °C for UPOP and Pd@UPOP, respectively. It was confirmed that the structure was not broken after loading of Pd

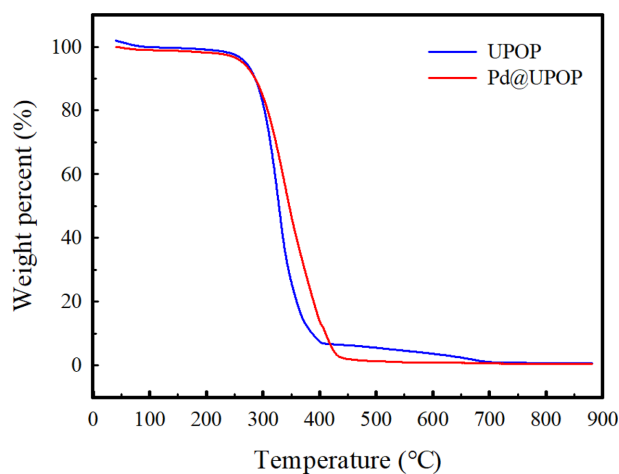
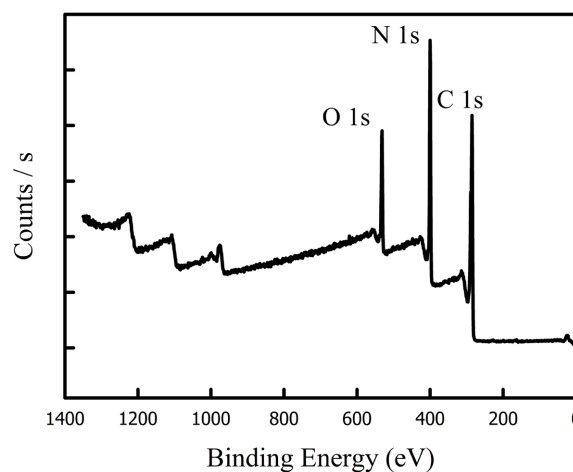


Figure 7. TGA thermograms of UPOP and Pd@UPOP catalyst under nitrogen atmosphere.

onto UPOP so that the decomposition temperature was the almost identical to pristine UPOP.

Elemental Analysis. XPS analysis was performed for elemental analysis and investigating interactions between palladium and other elements of Pd@UPOP shown in Figure 8



| Atom | Theoretical atomic percent (%) | Measured atomic percent (%) |
|------|--------------------------------|-----------------------------|
| C 1s | 55 | 58.45 |
| N 1s | 35 | 30.97 |
| O 1s | 10 | 10.58 |

Figure 8. XPS survey spectrum of UPOP and calculated element contents of carbon, nitrogen, and oxygen.

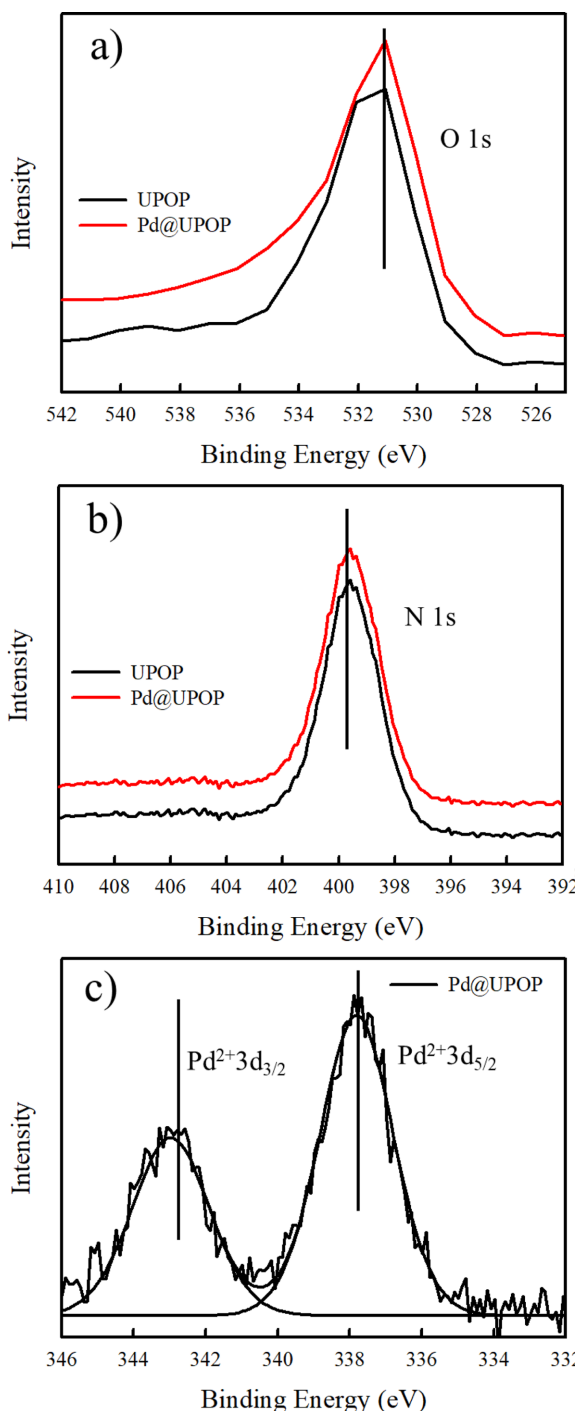


Figure 9. XPS (a) O 1s spectra of UPOP and Pd@UPOP; (b) N 1s spectra of UPOP and Pd@UPOP; (c) Pd 3d spectra of Pd@UPOP.

and Figure 9. From the survey spectrum for UPOP in Figure 8, measured atomic percents are almost the same as the theoretical value. In Figure 9, the binding energy of N 1s of UPOP and Pd@UPOP was shown at 399.6 eV. The binding

energy of O 1s of UPOP and Pd@UPOP was 531.05 eV. There is a slight shift of O is about in UPOP and Pd@UPOP due to the interactions of Pd with the frameworks.²¹ The peak of Pd 3d_{3/2} was shown at 337.81 eV and Pd 3d_{5/2} of Pd@UPOP was at 343.01 eV, respectively. The peak of Pd@UPOP was assigned to the +2 oxidation state. Furthermore, compared with Pd(OAc)₂ (338.40 eV),³³ the shift of 0.59 eV occurred for Pd@UPOP. It is assumed that this phenomenon is caused because Pd is immobilized on the surface of the polymer as reported elsewhere.²¹ As a result of the above data, it is confirmed that Pd is successfully immobilized in/onto the polymer. To further study of the exact amounts of immobilized Pd, ICP-OES analysis was carried out. ICP-OES confirmed that the amount of Pd of UPOP was 0.96 wt%. It is the expected result that Pd@UPOP contains a larger amount of Pd because it has sufficient nitrogen atoms to coordinate with Pd in the structure and internal space in the polymer in which Pd can penetrate inside the pores.

Catalytic Performance of Suzuki-Miyaura Cross-coupling Reaction. Suzuki-Miyaura reaction of 4-bromoanisole with phenylboronic acid was chosen for optimizing condition of catalytic performance. Table 1 lists the yield data of optimization study of Pd@UPOP. When the reaction of 4-bromoanisole with phenylboronic acid was performed with base in the presence of 0.1 mol% of Pd@UPOP, the reaction was carried out at 80 °C under aerobic condition for 1 h. To find optimum reaction condition, the reaction was performed with different bases and solvents. Pd@UPOP shows the highest performance of reaction in H₂O/EtOH (3:1 v/v). Among the bases such as NEt₃, KOH, K₂CO₃, and K₃PO₄, satisfactorily high enough yields were achieved for K₂CO₃ and K₃PO₄ (Table 1, entries 1-4). Further experiments were carried out to select solvents with K₂CO₃. The solvents tested were H₂O, EtOH, DMF and their mixtures. Test results showed that both Pd@UPOP had the highest yield when a mixture of water and ethanol in a ratio of 3: 1 v/v was used as a solvent. Especially, Pd@UPOP with K₂PO₃ showed a performance of 95% under the above conditions (entry 4). Because 4-bromoanisole having methoxy group is so electron-rich that the reaction is difficult to proceed. However, Pd@UPOP containing only 0.1 mol% Pd can reach 95% yields under aerobic condition for 1 h. As a result, Pd@UPOP with the best yield condition was chosen for further experiment with other aryl and heteroaryl bromides.

Catalytic performances of Pd@UPOP were evaluated for cross-coupling reaction with aryl and heteroaryl bromides as

Table 1. Optimization of the Suzuki-Miyaura Cross-coupling Reaction of 4-Bromoanisole with Phenylboronic Acid Catalyzed by Pd@UPOP

Reaction scheme: 4-bromoanisole + phenylboronic acid $\xrightarrow[\text{Solvent, Base, 80}^\circ\text{C}]{\text{Pd@UPOP}}$ 4-methoxybiphenyl

| Entry | Catalyst [0.1 mmol%] | Base | Solvent (mL) | Yield (%) |
|-------|-------------------------|--------------------------------|-----------------------------|-----------|
| 1 | | NEt ₃ | H ₂ O/EtOH (3:1) | 28 |
| 2 | | KOH | H ₂ O/EtOH (3:1) | 35 |
| 3 | | K ₂ CO ₃ | H ₂ O/EtOH (3:1) | 95 |
| 4 | | K ₃ PO ₄ | H ₂ O/EtOH (3:1) | 93 |
| 5 | | K ₂ CO ₃ | H ₂ O | 33 |
| 6 | | K ₂ CO ₃ | EtOH | 15 |
| 7 | | K ₂ CO ₃ | H ₂ O/EtOH (2:2) | 66 |
| 8 | UPOP | K ₂ CO ₃ | H ₂ O/DMF (2:2) | 59 |
| 9 | | K ₂ CO ₃ | H ₂ O/DMF (3:1) | 89 |
| 10 | | K ₃ PO ₄ | H ₂ O | 46 |
| 11 | | K ₃ PO ₄ | EtOH | 23 |
| 12 | | K ₃ PO ₄ | H ₂ O/EtOH (2:2) | 31 |
| 13 | | K ₃ PO ₄ | H ₂ O/DMF (2:2) | 35 |
| 14 | | K ₃ PO ₄ | H ₂ O/DMF (3:1) | 35 |

listed in Table 2. To examine the capability of Pd@UPOP as a catalyst, we divided the experiment sets into three classes. In the first group (Table 2, entries 1-4), the reaction was preceded with aryl bromide having electron donating group (EDG). For the second group (entries 5-8), aryl bromides have electron withdrawing group (EWG). The third group is heteroaryl bromides (9-11). Additionally, the reaction was carried out with benzene (entry 7). It is well-known that aryl bromides with EDG are more difficult for Suzuki-Miyaura cross-coupling reaction than bromobenzene. Because functional groups attached to the benzene ring push the electron to the benzene ring, the benzene ring is in an electron-rich state, so the reactant is stabilized.³⁴

However, Pd@UPOP works as an excellent catalyst for aryl bromides with EDG. For the investigation of steric effect, -OCH₃ in ortho and para position (entries 1-2) and -CH₃, in ortho and para position (entries 3-4) were compared. For both cases, the yield was greater for ortho-substituted aryl bromide due to steric hindrance. Also, -CH₃ substituted aryl bromide has a higher yield than -OCH₃ substituted one since -CH₃ is a weaker EDG than -OCH₃. This means the more electron rich in the benzene ring, the more difficult reaction proceeds.

Reaction with aryl bromides with EWGs such as 1-bromo-4-nitrobenzene, 4-bromobenzonitrile and 4-bromoacetophenone provided yields almost 100% (entries 6-8). EWGs pull the electrons from the benzene ring, which makes the benzene ring unstable. Then the unstable aryl bromides will readily react so yields become higher than EDGs.

The last reaction group is heteroaryl bromides having pyridinic group (entries 9-10) and thiophene (entry 11). The reaction with 3-bromopyridine produced the product in 97% yield (entry 10). However, yield for 2-bromopyridine was 71%, (entry 9). This result suggests that the closer heteroatom to Br makes the reaction more difficult. Furthermore, yields for 2-bromothiophene reached 100% (entry 11) because the electron density is lower in the benzene ring due to a lower electronegativity of S than that of N. It is generally known that heteroatoms in the benzene ring make the reaction difficult to proceed because of the high electron density in the ring. However, all of the reactions with aryl bromide reached above 90% within 1 h and the reaction with heteroaryl bromide reached at least 70% within 3 h. This is a remarkable result representing that Pd@UPOP is a highly efficient catalyst for Suzuki-Miyaura cross-coupling reaction.

Table 2. Suzuki-Miyaura Cross-coupling Reaction of Aryl Bromides and Heteroaryl Bromides with Phenylboronic Acid Catalyzed by Pd@UPOP in Water/EtOH

| Entry | Aryl bromide | | Product | Time (h) | Yield (%) |
|-------|------------------------|-----------|---------|----------|-----------|
| | Name | Structure | | | |
| 1 | 4-bromoanisole | | | 1 | 95 |
| 2 | 2-Bromoanisole | | | 1 | 91 |
| 3 | 4-Bromotoluene | | | 1 | 99 |
| 4 | 2-Bromotoluene | | | 1 | 97 |
| 5 | Bromobenzene | | | 1 | 100 |
| 6 | 1-Bromo-4-nitrobenzene | | | 1 | 100 |
| 7 | 4-Bromobenzonitrile | | | 1 | 100 |
| 8 | 4-Bromoacetophenone | | | 1 | 100 |
| 9 | 2-Bromopyridine | | | 3 | 71 |
| 10 | 3-Bromopyridine | | | 3 | 97 |
| 11 | 2-Bromothiophene | | | 3 | 100 |

Reactions were carried out by using aryl bromide (0.2 mmol), phenylboronic acid (0.24 mmol), K_3PO_4 (0.2 mmol), and [Pd] (0.1 mmol%) in solvent 4 mL (H_2O : EtOH 1:3 (v/v)). Reactions were carried out in air.

This high catalytic activity is assumed to be due to two reasons. First, UPOP has a large amount of N content (31%), so it can support sufficient palladium atoms in frameworks. Another reason is the high surface area of UPOP that enables palladium can be well dispersed on a wider area so it provides plentiful sites for the reaction.

Recyclability of Catalysts. The capability of recycling is a significant issue of heterogeneous catalysts. The catalytic recyclability of Pd@UPOP was evaluated by examining the reaction between 4-bromoanisole and phenylboronic acid. The

reaction was carried out under the condition of entry 1 in Table 2. After the reaction, the catalyst was centrifuged with ethanol for separated from products and dried in vacuum oven during 1 h for recovering the catalyst. Subsequently, next reaction was performed with recovered catalyst under the same condition. Figure 10 shows that catalyst performance marginally decreased with repeated runs due to the possible aggregation of Pd on the UPOP. At 5th run, the yield was 90% which is an encouraging result, implying that it can be sufficiently used as a heterogeneous catalyst.

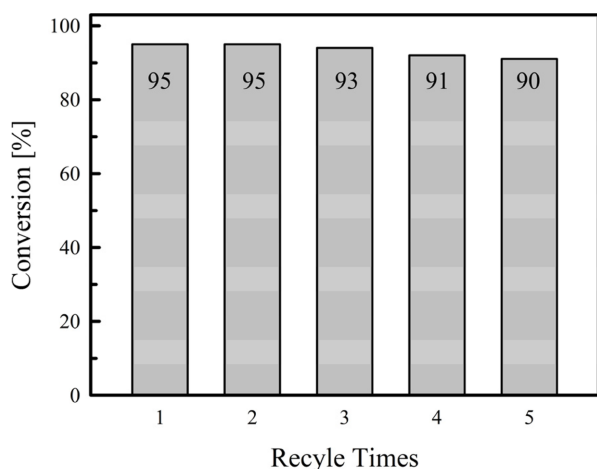


Figure 10. Recycling performance of Pd@UPOP catalyst in Suzuki-Miyaura cross-coupling reaction. Reaction conditions: 4-bromoanisole (2 mmol), phenyl boronic acid (2.4mmol), K_2CO_3 (2 mmol), [Pd] (0.1 mmol%) in solvent 4 mL ($H_2O:EtOH$ 3:1 v/v) at 80 °C for 1 h and reaction was carried out in air.

Conclusions

POPs based on polyurea, UPOP is successfully synthesized by condensation reaction. Its surface area, porosity, and thermal stability are enough to be used as catalyst supports. Since the UPOP is nitrogen-rich, they can hold Pd as to be efficient heterogeneous catalysts for Suzuki-Miyaura cross-coupling reaction. When Suzuki-Miyaura cross-coupling reaction is carried out with 4-bromoanisole and phenylboronic acid, the optimum conditions for both catalysts are the mixture of water/ethanol (3/1) as the solvent with K_2CO_3 as a base. Under these conditions, the yield of coupling reaction using Pd@UPOP is 95%. Especially, the coupling reaction using Pd@UPOP achieves above 100% yield when reacted with EWG and also acquires satisfactory catalytic performance even when reacted with EDG and heteroaryl halides. Considering the reaction conditions with only 0.1 mol% of Pd under aerobic condition for 1 h, it is a promising result. Furthermore, when Pd@UPOP is reused upto five times, the yield maintains above 90%, which is an excellent performance as a heterogeneous catalyst.

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References

1. Y. Zhang and S. N. Riduan, *Chem. Soc. Rev.*, **41**, 2083 (2012).
2. R. Gomes, P. Bhanja, and A. Bhaumik, *Chem. Commun.*, **51**, 10050 (2015).
3. V. Guillerm, Ł J. Weseliński, M. Alkordi, M. I. H. Mohideen, Y. Belmabkhout, A. J. Cairns, and M. Eddaoudi, *Chem. Commun.*, **50**, 1937 (2014).
4. Q. Chen, J. Wang, F. Yang, D. Zhou, N. Bian, X. Zhang, C. Yan, and B. Han, *J. Mater. Chem.*, **21**, 13554 (2011).
5. L. Xie and M. P. Suh, *Chemistry-A Eur. J.*, **19**, 11590 (2013).
6. O. K. Farha, A. M. Spokoyny, B. G. Hauser, Y. Bae, S. E. Brown, R. Q. Snurr, C. A. Mirkin, and J. T. Hupp, *Chem. Mater.*, **21**, 3033 (2009).
7. O. K. Farha, Y. Bae, B. G. Hauser, A. M. Spokoyny, R. Q. Snurr, C. A. Mirkin, and J. T. Hupp, *Chem. Commun.*, **46**, 1056 (2010).
8. X. Zhu, S. M. Mahurin, S. An, C. Do-Thanh, C. Tian, Y. Li, L. W. Gill, E. W. Hagaman, Z. Bian, and J. Zhou, *Chem. Commun.*, **50**, 7933 (2014).
9. C. D. Wood, B. Tan, A. Trewin, F. Su, M. J. Rosseinsky, D. Bradshaw, Y. Sun, L. Zhou, and A. I. Cooper, *Adv. Mater.*, **20**, 1916 (2008).
10. Y. Xie, T. T. Wang, X. H. Liu, K. Zou, and W. Q. Deng, *Nat. Commun.*, **4**, 1960 (2013).
11. S. Bhunia, N. Chatterjee, S. Das, K. Das Saha, and A. Bhaumik, *ACS Appl. Mater. Interf.*, **6**, 22569 (2014).
12. S. H. Wibowo, A. Sulistio, E. H. Wong, A. Blencowe, and G. G. Qiao, *Adv. Funct. Mater.*, **25**, 3147 (2015).
13. Y. Xu, L. Chen, Z. Guo, A. Nagai, and D. Jiang, *J. Am. Chem. Soc.*, **133**, 17622 (2011).
14. A. Patra and U. Scherf, *Chem. Eur. J.*, **18**, 10074 (2012).
15. A. Köhler, J. S. Wilson, and R. H. Friend, *Adv. Eng. Mater.*, **4**, 453 (2002).
16. P. Kaur, J. T. Hupp, and S. T. Nguyen, *ACS Catalysis*, **1**, 819 (2011).
17. L. M. Bronstein, G. Goerigk, M. Kostylev, M. Pink, I. A. Khotina, P. M. Valetsky, V. G. Matveeva, E. M. Sulman, M. G. Sulman, and A. V. Bykov, *J. Phys. Chem. B*, **108**, 18234 (2004).
18. T. Hasell, C. D. Wood, R. Clowes, J. T. Jones, Y. Z. Khimyak, D. J. Adams, and A. I. Cooper, *Chem. Mater.*, **22**, 557 (2009).
19. X. Du, Y. Sun, B. Tan, Q. Teng, X. Yao, C. Su, and W. Wang, *Chem. Commun.*, **46**, 970 (2010).
20. J. Jiang, C. Wang, A. Laybourn, T. Hasell, R. Clowes, Y. Z. Khimyak, J. Xiao, S. J. Higgins, D. J. Adams, and A. I. Cooper, *Angew. Chem. Inter. Ed.*, **50**, 1072 (2011).
21. L. Li, Z. Chen, H. Zhong, and R. Wang, *Chem. Eur. J.*, **20**, 3050 (2014).
22. K. Billingsley and S. L. Buchwald, *J. Am. Chem. Soc.*, **129**, 3358 (2007).
23. T. Hoshi, I. Saitoh, T. Nakazawa, T. Suzuki, J. Sakai, and H. Hagiwara, *J. Org. Chem.*, **74**, 4013 (2009).
24. A. Minato, K. Tamao, T. Hayashi, K. Suzuki, and M. Kumada,

- Tetrahedron Lett.*, **22**, 5319 (1981).
25. N. Shahnaz, B. Banik, and P. Das, *Tetrahedron Lett.*, **54**, 2886 (2013).
26. I. D. Kostas, B. R. Steele, A. Terzis, S. V. Amosova, A. V. Martynov, and N. A. Makhaeva, *Eur. J. Inorg. Chem.*, **2006**, 2642 (2006).
27. B. Banik, A. Tairai, N. Shahnaz, and P. Das, *Tetrahedron Lett.*, **53**, 5627 (2012).
28. M. Navidi, N. Rezaei, and B. Movassagh, *J. Organomet. Chem.*, **743**, 63 (2013).
29. T. Mino, Y. Shirae, M. Sakamoto, and T. Fujita, *J. Org. Chem.*, **70**, 2191 (2005).
30. T. Mino, Y. Shirae, M. Sakamoto, and T. Fujita, *Synlett*, **2003**, 0882 (2003).
31. B. Tao and D. W. Boykin, *J. Org. Chem.*, **69**, 4330 (2004).
32. N. Rangel-Vazquez, C. Sánchez-López, and F. R. Felix, *Polímeros*, **24**, 453 (2014).
33. L. Yang, Y. Tang, D. Yan, T. Liu, C. Liu, and S. Luo, *ACS Appl. Mater. Interf.*, **8**, 169 (2015).
34. M. Kutubi, K. Sato, K. Wada, T. Yamamoto, S. Matsumura, K. Kusada, H. Kobayashi, H. Kitagawa, and K. Nagaoka, *ChemCatChem*, **7**, 3887 (2015).