

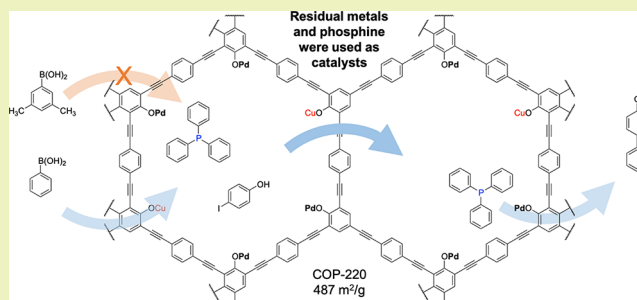
Sustainable Porous Polymer Catalyst for Size-Selective Cross-Coupling Reactions

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Supporting Information

ABSTRACT: A new, high surface area, nanoporous polymer (COP-220) was synthesized using sustainable building blocks, namely, a food coloring dye (erythrosine B) and a commercial alkyne. During the Sonogashira coupling, it is observed that Pd and Cu ions and triphenylphosphine ligands of the catalyst get trapped inside the pores. The remnant synthesis catalyst components were characterized in detail and were tested as a new catalyst for Suzuki–Miyaura coupling reactions. COP-220 showed conversion yields comparable to the commercial homogeneous catalyst Pd(PPh₃)₂Cl₂ with an additional advantage of size-dependent catalytic activity when bulkier substrates were used. COP-220 was highly stable under thermal and chemical treatments and recyclable with no loss of activity. These findings show a clear need for extensive characterization of nanoporous polymers made through cross-coupling reactions and the potential of the trapped catalysts for new catalytic activity without additional loading.

KEYWORDS: Microporous materials, Porous polymers, Solid-state catalysis, Residual reagents, Size-selective catalysis



INTRODUCTION

Solid catalysts offer easy separations and recovery for reuse, and their enhanced thermal and chemical stability in the solid state favor their industrial adaptations compared to the solution-dispersed versions.^{1–3} Porosity plays an important role in effective substrate delivery, and nanoporous polymers combine their robust nature with easy diffusion for great promise in catalytic transformations.

One important catalytic reaction is the Suzuki coupling for C–C bond making, and traditionally, Pd-based homogeneous catalysts dominated the applications.⁴ In contrast to conventional palladium catalysts, solid catalysts for Suzuki coupling are usually composed of the active palladium metal part and its support. To increase the contact surface and yields, inert materials with high surface area and stability are frequently used as supports, such as graphene⁵ and metal–organic frameworks (MOFs),^{6–12} and porous organic materials.^{13–20} Among them, porous organic materials are particularly intensively studied mainly due to their high structural tunability,²¹ which can also allow their application for catalysis,^{22–28} CO₂ capture,^{29–35} CO₂ conversion,^{36–39} and pollutant removal.^{40–44} For example, Ding et al. reported a

Pd(II)-containing covalent organic framework (COF) named Pd/COF-LZU1 for Suzuki coupling.¹³ Li et al. reported microporous knitting aryl network polymers (KAPs) with benzene, triphenylphosphine (PPh₃), and palladium to make KAPs(Ph-PPh₃)-Pd to be used in heterogeneous Suzuki coupling reactions.¹⁴ Furthermore, Li et al. used a metal-losalen-based microporous organic polymer (MsMOP-1) to make a palladium-incorporated structure and reported high yields.¹⁵ These, however, introduce palladium post-synthetically, and the distribution over the framework structure is not always uniform. The use of excessive catalyst and solvents for impregnation also hinders their feasibility. In addition, the porous supports are made from custom-made linkers, adding to the complexity in widespread implementation. An atom economical heterogeneous catalyst design that uses widely available or natural building blocks is necessary.

To achieve sustainability in solid polymer catalysts, reducing the use of nonessential reagents or solvents is crucial. Commercial chemicals as monomers allow the synthesis to

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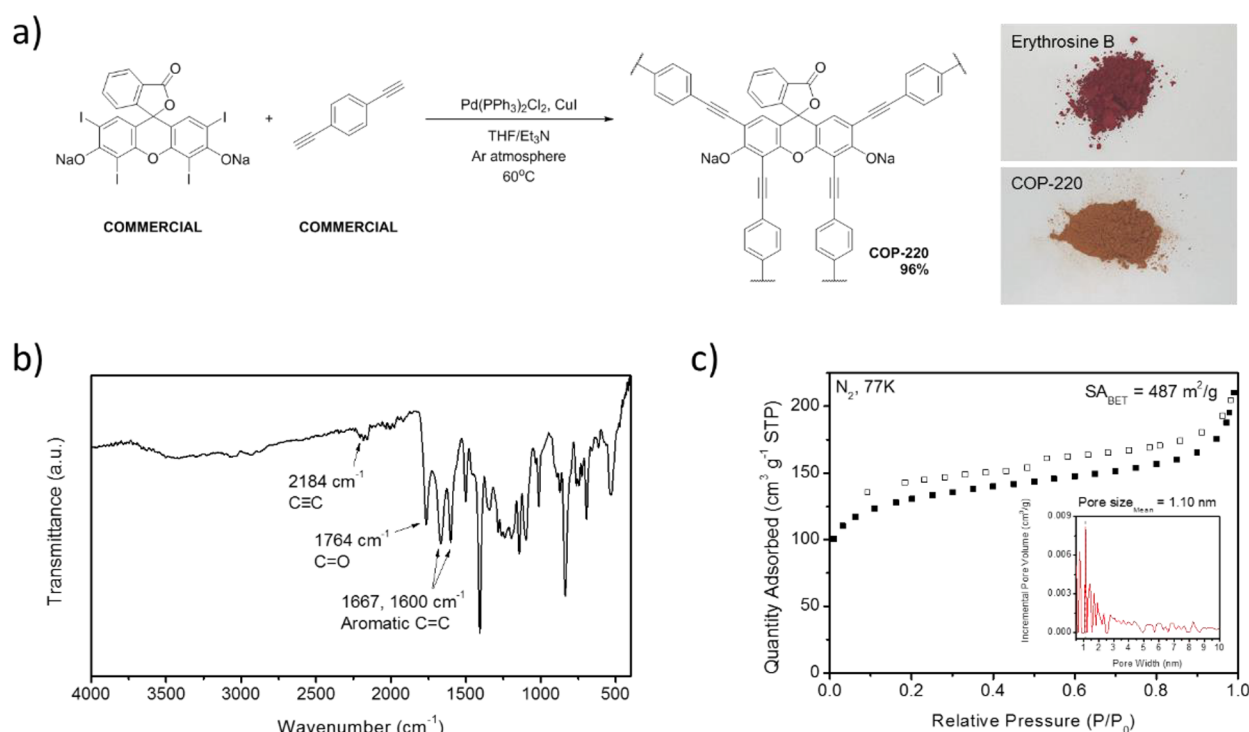


Figure 1. Synthesis and characterization of COP-220. (a) Synthetic scheme, (b) FT-IR spectra, and (c) nitrogen (77 K) physisorption isotherm of COP-220. Inset: pore size distribution calculated by NLDFT.

be much greener by dropping synthetic complexity. The switchover to already used materials which remain in the reaction system for other purposes can be another approach for sustainability by adopting the concept of recycling. Furthermore, it is known that a trace amount of metals can catalyze coupling reactions.^{45,46} The application of trace-metal catalysis to porous polymer catalysts could further contribute to an increase in sustainability.

In this study, we report an easy, one-pot, and readily scalable synthesis of Pd-based heterogeneous catalyst (COP-220, COP stands for covalent organic polymer) from commercially available building blocks by Sonogashira coupling. Erythrosine B, a food coloring dye and a biological stain that is widely available, was used as the core building block of COP-220. It was discovered that COP-220 contained residual palladium (0.35 wt %), copper (0.13 wt %), and triphenylphosphine (1.95 wt %, from XPS). To the best of our knowledge, this is the first time all three components were observed in cross-coupling-based nanoporous polymers. We then repurposed these contaminants for Suzuki coupling to achieve high yield conversions with great chemical group tolerance. Furthermore, we also employed the pore confinement of the nanoporous polymer to show size dependence for a selective Suzuki coupling. Partial heterogeneity of COP-220 in catalysis was examined through a filtration procedure and a three-phase test. COP-220 also showed no degradation under elevated temperatures, acid/base treatments, and storage in air, allowing for catalyst recycling for at least several cycles.

RESULTS AND DISCUSSION

COP-220 is prepared by a one-pot Sonogashira coupling of commercial building blocks, namely, erythrosine B and 1,4-diethynyl benzene, in 96% yield (Figure 1). Erythrosine B is a commercial red dye, which is produced by iodination of a

widely available dye, fluorescein. It is also known as Red No. 3, which is mainly used for food coloring. Incorporation of this edible dye into the porous network allows COP-220 to provide accessibility, scalability, synthetic sustainability, and nontoxic unreacted left-over monomers. Due to the innate red color of erythrosine B, COP-220 displayed a red-brown powder. More synthetic details are described in the [Experimental Section](#).

COP-220 formation was verified by Fourier transform infrared spectroscopy (FT-IR) (Figure 1b). In the FT-IR spectrum, the characteristic peak of the internal carbon–carbon triple bond (C≡C) stretching is shown around 2184 cm^{-1} . This indicates the formation of a new carbon–carbon bond, which connects erythrosine B and 1,4-diethynylbenzene. Moreover, the C=O from the ester moiety in erythrosine B matches to the peak around 1764 cm^{-1} . A variety of aromatic carbon–carbon bonds present in the super structure yield the signals at 1667 and 1600 cm^{-1} . The thermal stability of COP-220 was measured with thermogravimetric analysis (TGA) under air and N_2 atmosphere (Figure S1). Under both inert and oxidative environments, COP-220 was stable up to at least 300 °C. Also, COP-220 was found amorphous by powder X-ray diffraction measurements (Figure S2).

The porosity of COP-220 was studied by N_2 physisorption measurements at 77 K (Figure 1c). It was found to be mainly microporous with a commonly observed hysteresis due to the delay of the probe gas in exiting the microporous framework.⁴⁷ The Brunauer–Emmett–Teller (BET) surface area was 487 $\text{m}^2 \text{g}^{-1}$, and the total pore volume was 0.182 cm^3/g . Rouquerol plots and pressure regimes for BET surface area calculation are included in Figure S5. Pore size distribution was calculated by nonlocal density functional theory (NLDFT) with slit pore approximation. Pores are mainly in the microporous area (less than 2.0 nm), with the average pore diameter of 1.10 nm. In the synthesis of COP-220, the molar ratio between erythrosine

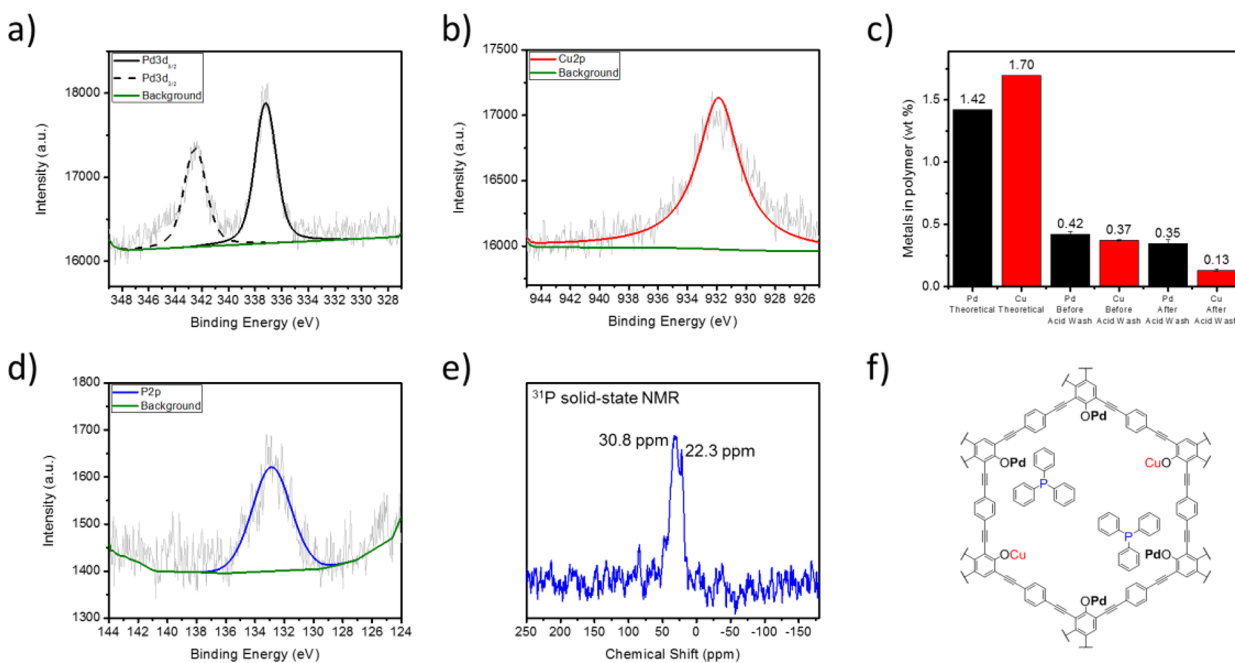


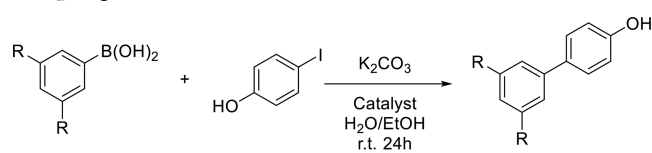
Figure 2. Characterization of the residual reagents in COP-220. (a) XPS spectra of Pd 3d. (b) XPS spectra of Cu 2p. (c) ICP-MS data for Pd and Cu at theoretical amounts, before the acid wash, and after the acid wash. (d) XPS spectra of P 2p. (e) Solid-state ³¹P NMR. (f) A possible schematic of the pore contents discovered in the residual element analysis.

B and 1,4-diethynylbenzene was varied from 1:2 to 1:4 to optimize the ratio with the highest surface area. Among them, porous polymer with the ratio of erythrosine B to 1,4-diethynylbenzene as 1:4 showed the highest surface area (Figure S3), which was used in this study as the standard protocol to make COP-220.

To investigate the residual reagents in Sonogashira coupling, X-ray photoelectron spectroscopy (XPS), inductively coupled plasma mass spectrometry (ICP-MS), and solid-state ³¹P NMR measurements were carried out (Figure 2). XPS analysis showed peaks at 337.2 and 342.5 eV (Figure 2a), which correspond to Pd 3d_{5/2} and Pd 3d_{3/2}, respectively. These exactly match with palladium oxide,⁴⁸ indicating that the palladium metal is mainly coordinated to the oxygen atom in the erythrosine B moiety, with a 2+ oxidation state (Figure 2f). The signal at 931.9 eV commonly corresponds to Cu 2p (Figure 2b). Considering that elemental copper shows a peak at 932.7 eV and the signal for Cu(I) is located in the lower binding energy region,^{49,50} it is clear that the copper exists as the 1+ oxidation state in the porous network, most likely tethered to the phenolates similar to Pd. Quantification of these metals is done with ICP-MS (Figure 2c). Assuming that every metal used for COP-220 synthesis is embedded inside the pores, palladium and copper should have 1.42 and 1.70 wt % in the overall composition. Since the acid washing step in the workup process of COP-220 synthesis aims at the removal of excess reagents, particularly the remaining metals, COP-220 was analyzed before and after the acid wash. It contained 0.42 wt % of palladium and 0.37 wt % of copper before the acid wash (Figure 2c). After COP-220 was intensely washed with a 1 M HCl solution after stirring in the solution for 2 days, 0.35 wt % of palladium and 0.13 wt % of copper remained. Compared to the sample before the acid wash, 83% palladium and 35% copper seem to remain. This shows that palladium is trapped inside the porous network more than copper, possibly by strongly coordinating with oxygen atoms in the network as

described in the XPS analysis. In contrast to palladium and copper, no evidence for residual sodium from erythrosine B was observed in the XPS study. In addition to the residual metals, triphenylphosphine (PPh₃) from the Pd(PPh₃)₂Cl₂ catalyst was also analyzed. To the best of our knowledge, none of the reports on coupling-based nanoporous polymer synthesis looked into these possibilities. In XPS analysis, a P 2p peak was observed at 132.9 eV. Although the signal is low for exact deconvolution of the spectra, it mainly conforms with the form of triphenylphosphine oxide (Ph₃PO).⁵¹ This is why we looked into solid-state ³¹P NMR for a clear identification (Figure 2e). Two distinct peaks were observed at 22.3 and 30.8 ppm. To characterize these peaks, ³¹P NMR spectra were also obtained for PPh₃, Pd(PPh₃)₂Cl₂, and triphenylphosphine oxide (Ph₃PO) (Figure S4). PPh₃ showed a signal at -9.4 ppm, but its complexation with palladium (Pd(PPh₃)₂Cl₂) shifted the peak to 21.4 ppm. Ph₃PO, a representative waste product from PPh₃ mainly thought to be originated by aerobic oxidation during the washing steps, resulted in a signal of 26.6 ppm. On the basis of these measurements, it could be suggested that residual triphenylphosphine exists as either a palladium-complexed state (22.3 ppm) or oxidized state (30.8 ppm), with a slight shift downfield due to the interaction of Pd-PPh₃ or Ph₃PO with the dangling phenolate oxygens of the polymer.

After the residual reagents inside the pore were quantified, COP-220 was used as a heterogeneous catalyst for Suzuki coupling without adding any additional catalyst. The reaction of 4-iodophenol and boronic acid (phenylboronic acid or 3,5-dimethylphenylboronic acid) was chosen as a model reaction (Table 1) for two circumstances: (1) the standard reaction with no solubility problems and (2) the methyl substitution would allow us to check whether size-selective transformation is possible. COP-220 was used as the only catalyst, and Pd(PPh₃)₂Cl₂ was set as a control, which was also the homogeneous catalyst used in the synthesis of COP-220. The

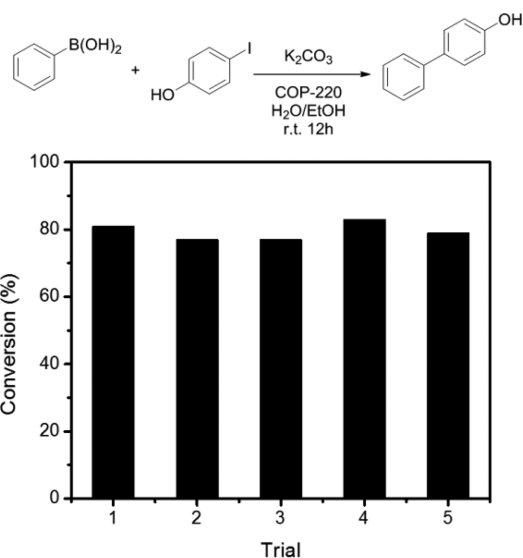
Table 1. Catalytic Activity Test of COP-220 for Suzuki Coupling^a


entry	R	catalyst type	catalyst loading (mol %)	yield (%) ^b
1	H	Pd(PPh ₃) ₂ Cl ₂	0.1	87
2	H	COP-220	0.1	85
3	CH ₃	Pd(PPh ₃) ₂ Cl ₂	0.1	93
4	CH ₃	COP-220	0.1	93
5	H	Pd(PPh ₃) ₂ Cl ₂	0.02	48
6	H	COP-220	0.02	40
7	CH ₃	Pd(PPh ₃) ₂ Cl ₂	0.02	41
8	CH ₃	COP-220	0.02	22

^aReaction conditions: catalyst (0.02–0.1 mol %), boronic acid (1 mmol), iodophenol (1 mmol), and K₂CO₃ (3 mmol). ^bConversions were determined using ¹H NMR.

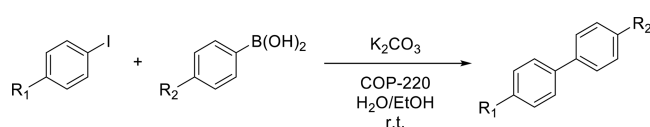
catalyst amount was varied from 0.1 to 0.02 mol % to observe catalyst amount dependence. When 0.1 mol % catalyst was used, the yield was moderately high (85% to 93%) regardless of the type of boronic acid or catalyst (entries 1 to 4). This high yield suggests that 0.1 mol % catalyst is enough for the reaction. It is remarkable that the remnant Pd could carry out the conversion without any further treatment or additives. However, the decrease of catalyst amount resulted in a reactivity difference. For 0.02 mol % catalyst, the product was obtained at 48% for Pd(PPh₃)₂Cl₂ (entry 5) and 40% for COP-220 (entry 6) when unhindered phenylboronic acid was used. In the case of the replacement of the phenylboronic acid to bulkier 3,5-dimethylphenylboronic acid, the yield dropped from 41% to 22% with the change of catalyst from Pd(PPh₃)₂Cl₂ to COP-220 (entries 7 and 8). Substrate size difference is most likely the main reason for this abrupt drop in yield. Since the average pore diameter of COP-220 is calculated to be 1.10 nm, which is only slightly larger than the product formed in the model reactions, the bulkier substrate has, therefore, less accessibility to the pores and, namely, the metal catalysts inside them. Bulkier product has less tendency to escape from the pores, which also blocks new substrate to come in for the reaction. In other words, a bulkier substrate makes the usability of a pore-confined catalyst challenging, causing the reaction to predominantly happen on the metals near the surface of COP-220. In entry 4, where a higher catalyst loading (0.1 mol %) was used, palladiums on the surface of COP-220 were enough to push the reaction forward since the yield was similar to homogeneous catalyst (Pd(PPh₃)₂Cl₂).

A major advantage of a heterogeneous catalysis is the ease of separating used catalysts and applying them again for a new reaction. To check the recyclability of the reaction, catalysts were separated after the reaction was finished, rinsed with ethanol, and reused in further reactions as a recycled catalyst. The catalytic activity of COP-220 was maintained for up to 5 cycles tested (Figure 3). In all five successive recycling tests, the conversion rate was between 77% and 83%. This reusability also suggests the chemical stability of COP-220 to organic solvents, dry conditions, and acid/base treatments. Palladium on carbon, a popular heterogeneous palladium catalyst, is

**Figure 3. Recycling test of COP-220.**

known to be pyrophoric especially when it is used on a large scale under air.^{52,53} COP-220 could be one safe alternative to palladium on carbon for Suzuki coupling.

To observe the versatility of COP-220 as a catalyst for Suzuki coupling, several substrates with different functionalities were tested (Table 2). For all the substrates tested, the yield

Table 2. Substrate Scope Screening for Suzuki Coupling with COP-220 as a Catalyst


entry	R ₁	R ₂	conversion (%)
1	H	H	85
2	CH ₃	H	92
3	OCH ₃	H	89
4	NO ₂	H	95
5	3,5-diCH ₃	H	93
6	naph	H	84
7	H	COOCH ₃	77

was in the range of moderate to high. When iodobenzenes with para-substitution were reacted with phenylboronic acid under COP-220, the conversion was higher than 85%. Even the use of naphthalene as a halide resulted in a moderate yield of 84% regardless of the bulkiness of the substrate (entry 6). This reaction also worked for a different boronic acid, so that the yield was still in the moderate range.

Solid catalysts are known to work in two different mechanisms. In heterogeneous catalysis, metals are chemically bound to the catalyst framework so that the reactants approach the catalytic components for the reaction to proceed. However, if the metals are not strongly bound to the network structure, they could leach into the reaction mixture, leading to a homogeneous catalysis. To check how COP-220 catalyzes the reaction in either a heterogeneous or homogeneous manner, two kinds of tests were performed. First, COP-220 was separated from the reaction mixture by filtration during the reaction (filtration procedure, see the Experimental Section for

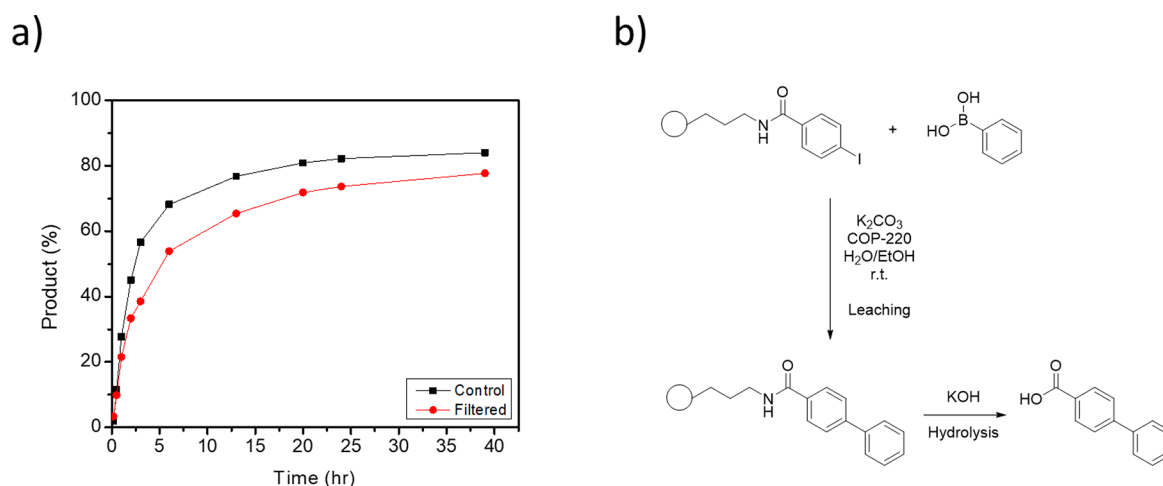


Figure 4. Tests for leaching of metals in the reaction catalyzed by COP-220. (a) Comparison of the conversion rate from the filtration test (black, control; red, solids were filtered). (b) Three-phase test and the expected product from leaching.

details).⁵⁴ When the filtrate was stirred further, the conversion rate dropped but continued to increase (Figure 4a), suggesting that the leached metals in the reaction mixture further catalyzed the product formation. However, compared to the control in which COP-220 was not filtered, the increase of conversion rate was slower, indicating the partial heterogeneous property of COP-220-based catalysis. This concept was further examined with a three-phase test (Figure 4b).^{55,56} For this test, 3-aminopropyl functionalized silica was modified under the reaction with 4-iodobenzoyl chloride, introducing an iodide group. Iodide-immobilized silica was then reacted with phenylboronic acid under COP-220, so that the reaction could only be catalyzed by leached metals. After the reaction was finished, silica was hydrolyzed with a base to analyze the product. As expected from the filtration test above, leaching occurred, resulting in the coupled product. On the basis of the filtration procedure and the three-phase test above, it can be concluded that COP-220-dependent catalysis goes through both homogeneous and heterogeneous mechanisms.

CONCLUSIONS

In this work, we showed the synthesis of a new, nanoporous, heterogeneous, palladium-based catalyst COP-220 in a one-pot reaction from commercially available building blocks. The nanoporous polymer did not need addition of Pd to turn it into a coupling catalyst since it trapped all components of the Sonogashira coupling. This makes the COP-220 production process less polluting than impregnation-based Pd catalyst preparations. The use of food coloring dye, erythrosine B, also enables a sustainability component and for the repurposing of an already existing chemical commodity. The residual metals and triphenylphosphine were quantified and used for catalytic Suzuki coupling for several different substrates. Conversion efficiency changed by the substrate size, indicating the possible use of the porous network in size-selective coupling reactions. Furthermore, quantitative catalytic activity up to 5 cycles of reuse shows the chemical stability of COP-220. On the basis of the filtration procedure and the three-phase test, a partial heterogeneous catalytic process was observed for COP-220-based catalysis. We expect that this study will put more emphasis on nanoporous polymers for catalytic transformations and also show how the catalysts could be fixed in the superstructure.

EXPERIMENTAL SECTION

Materials and Characterization. Erythrosine B was purchased from Tokyo Chemical Industry (TCI) Co., Ltd., Japan. Anhydrous potassium carbonate and the solvents were purchased from Samchun Chemical Co., Ltd., South Korea. All of the other chemicals mentioned above were purchased from Sigma-Aldrich, USA. All chemicals and products were verified with ¹H NMR spectra obtained by a Bruker AVANCE 400 instrument. Fourier transform infrared spectroscopy (FT-IR) analysis was carried out in the ATR mode using a Shimadzu IRTracer-100 instrument. Nitrogen or argon gas physisorption isotherms were obtained using a Micromeritics 3-Flex surface characterization analyzer. Thermogravimetric analysis (TGA) was performed using a Netzsch TG209 F1 Libra instrument. Powder X-ray diffraction (PXRD) spectra were obtained with a Rigaku Smartlab apparatus. X-ray photoelectron spectroscopy (XPS) was carried out with a Thermo VG Scientific K-alpha model. Solid-state ³¹P NMR spectra were acquired with an Agilent NMR DD2 (9.4 T) instrument at a resonance frequency of 161.8 MHz. A 1.6 mm sample rotor was used, and its magic angle spinning (MAS) speed was 20 or 40 kHz. ³¹P direct detection was performed with a $\pi/6$ pulse width of 1 μ s (radio frequency strength of 100 kHz) with a recycle delay of 15 s and with more than 1000 accumulated transients. All peaks were referenced with 85% H₃PO₄ in H₂O solution as 0 ppm.

Synthesis of COP-220. In a one-neck 50 mL round-bottomed flask, erythrosine B (400 mg, 0.46 mmol), 1,4-diethynylbenzene (229 mg, 1.81 mmol), bis(triphenylphosphine)palladium(II) chloride (38 mg, 0.05 mmol), and copper(I) iodide (21 mg, 0.11 mmol) were added. Argon gas and a mixture of dry tetrahydrofuran and triethylamine (10 and 15 mL each) were added to create inert conditions. The reaction mixture was set to 60 °C and allowed to stir for 16 h. After the mixture was cooled to room temperature, the precipitate was filtered and washed with distilled water, methanol, and acetone. The resulting powder was dried at 100 °C under vacuum overnight, finely ground, and washed with a Soxhlet apparatus with methanol for 48 h. The remaining erythrosine B dye was eluted by the methanol wash. After drying, the resulting powder was washed with 1 M HCl solution for 2 days (HCl solution was changed twice in this washing step). The resulting powder was dried to yield COP-220 (380 mg, 96% yield based on repeated monomeric unit excluding residual reagents).

Catalytic Activity Test of COP-220. In a one-neck 25 mL round-bottomed flask, boronic acid (1 mmol), 4-iodophenol (220 mg, 1 mmol), anhydrous K₂CO₃ (414 mg, 3 mmol), and palladium catalyst (0.1 mol %) were added. A water and ethanol mixture (5 mL each) was added to the reaction mixture, and the resulting reaction mixture was stirred for 24 h at room temperature. The catalyst was filtered, and the ethanol was evaporated with a rotary evaporator; the product

was extracted with dichloromethane. The product was obtained after the evaporation of dichloromethane. For the 0.02 mol % catalytic loading, boronic acid and 4-iodophenol (5 mmol each) were added. For the recycling test, the catalyst separated after 12 h of reaction was rinsed with ethanol and directly reused for the next cycle.

Filtration Procedure. The reaction was set as mentioned in the **Catalytic Activity Test of COP-220** section above. After reaction for 10 min, the mixture was filtered with a syringe filter (0.45 μm). There was no observable COP-220 powder remaining in the filtrate. The filtrate was continuously stirred, and the reaction progress was monitored by sampling the reaction mixture at each specified time and analyzing the samples by NMR. For the control experiment, the same procedure proceeded without filtering COP-220.

Three-Phase Test. Iodide-modified silica was synthesized based on previous reports.^{54,57} Briefly, 4-iodobenzoyl chloride (3 mmol, 0.80 g) was reacted with 3-aminopropyl functionalized silica (1 mmol based on amine contents) in dry THF (10 mL) and pyridine (0.24 μL) at 40 °C under argon atmosphere for 12 h. After the solid was separated by centrifugation and washed with 5% (v/v) HCl, 0.02 M K_2CO_3 aqueous solution, water, and ethanol, it was further washed with DCM with a Soxhlet apparatus. The dried solid was analyzed with TGA analysis to verify the conversion (iodide concentration of 1 mmol/g based on TGA analysis).

Iodide-modified silica (1 mmol based on iodide) was reacted with phenylboronic acid under the reaction condition mentioned in the **Catalytic Activity Test of COP-220** section above. After the reaction finished, the solids were filtered and washed with ethanol. Remaining reagents were further washed with ethanol by a Soxhlet apparatus for 24 h. Then, a 2 M KOH solution in ethanol/water (10 mL/5 mL) was added to the silica, and the solution was stirred at 90 °C for 3 days to hydrolyze the product. The solution was neutralized with 10% HCl, extracted with dichloromethane, and analyzed with ^1H NMR.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b01729.

(Figure S1) TGA curves of COP-220 under air (black) or N_2 (red) flow; (Figure S2) powder X-ray diffraction pattern of COP-220; (Figure S3) argon physisorption isotherms of COP-220 at 77 K; (Figure S4) solid-state ^{31}P NMR spectra of phosphoric acid (H_3PO_4) as a reference, (b) triphenylphosphine (PPh_3), (c) bis(triphenylphosphine)palladium(II) dichloride ($\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$), and (d) triphenylphosphine oxide (Ph_3PO); (Figure S5) calculated Rouquerol plot for COP-220 along with the pressure ranges used for the BET surface area calculations (PDF)

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Notes

The authors declare no competing financial interest.

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